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THE PHOTOMETRIC DETERMINATION OF PALLADIUM  
WITH 4-(2-PYRIDYLAZO)RESORCINOL

A THESIS

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THE PHOTOMETRIC DETERMINATION OF PALLADIUM

WITH 4-(2-PYRIDYLAZO)RESORCINOL

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## SUMMARY

The determination of minor quantities of metals by spectrophotometric methods is a well-established technique. Although many metal ions are not sufficiently absorbing, spectrophotometric analysis is still possible. In such cases reagents are employed that form highly absorbing species with the desired metals. Often, however, more than one metal is capable of forming a colored product with a particular chromogenic reagent. This lack of selectivity is one of the major problems encountered in spectrophotometric analysis. While it is possible to frequently exclude the interference of some metals by the application of masking techniques, this is not a remedy for all cases. When it is impossible to mask an interference, then separations are necessary. The development of ion exchange, chromatography and solvent extraction techniques has made such separations much more practical; however, masking is still the preferred approach.

The spectrophotometric determination of palladium is an example where selectivity is an important problem. Over one hundred methods for the photometric determination of palladium have appeared in the literature. However, only about one-tenth of these methods have any degree of selectivity, and usually a prior separation is required to prevent interference by associated metals. The development of a method that would allow for the specific determination of palladium while maintaining high sensitivity and easy handling techniques is very desirable.

This research was undertaken to investigate the application of

4-(2-pyridylazo)resorcinol (PAR) as a possible specific and sensitive reagent for the spectrophotometric determination of palladium. In order to improve the selectivity of the method, the effects of pH and the presence of various masking reagents were investigated. Two basic approaches were developed, the first carried out at pH 7.0 and the second in a strongly acidic medium. These and several modifications have been evaluated and are described in detail.

#### Method at pH 7.0

The original approach was to carry out the reaction at pH 7.0 and to employ masking agents to improve the selectivity of the method. EDTA was evaluated first, but it was found that some metals were not masked under these conditions. Further investigation revealed that citrate was capable of masking many metals at this pH and it was decided to employ a solution containing both EDTA and sodium citrate for masking. While studying the influence of other ions on the palladium-PAR complex, chloride was found to have two effects. The first was a lowering of the absorptivity of the palladium-PAR complex, and the second was kinetic in nature. Both of these effects were concentration dependent, but it was found that if a certain minimum concentration of chloride was established, further increase in concentration of this ion had no effect. In order to simplify the procedural details, it was decided to include chloride in the masking solution. In addition to the masking action this solution served as a buffer to maintain the pH at about 7. Under these conditions, palladium forms a stable red complex with PAR, which has an absorption maximum at 516 m $\mu$ . The time required for the color development is about 30 minutes. The complex obeys Beer's law over the range 0 to

3.26  $\mu\text{g}$  palladium per milliliter. The molar absorptivity is  $2.9 \times 10^4$  and the sensitivity as expressed by Sandell is  $0.0038 \mu\text{g}/\text{cm}^2$ .

The method was found to give satisfactory results when determining palladium in pure solutions and in the presence of the following metals for concentration ratios as high as 2000:1 (metal to palladium): lithium, potassium, sodium, rubidium, cesium, magnesium, calcium, strontium, barium, aluminum, arsenic(III) and (V), scandium, yttrium, manganese, tungsten, zinc, cadmium, mercury(II), gallium, indium, thallium(I) and (III), tin(IV), lead, antimony(III) and (V), bismuth, selenium, lanthanum, praseodymium, neodymium, cerium(III), nickel, copper, chromium(III) and (VI), vanadium(IV), iron(III), ruthenium, and osmium. Uranyl ion can be masked by the addition of sodium carbonate.

Niobium, tantalum, cobalt, gold, silver, iridium, platinum, and vanadium(V) are not masked and interfere with this method. In the absence of these elements the method is rapid, accurate and sensitive.

#### Method in 3 F Sulfuric Acid

In an attempt to improve selectivity, the reaction of palladium with PAR was studied in 3 F sulfuric acid. Under these conditions a stable green-colored complex is formed. Two approaches were originally taken. In the first, the absorbance measurements were made in the aqueous sulfuric acid medium, while the second approach employed an extraction of the palladium-PAR complex into ethyl acetate. During these investigations a very interesting influence of chloride was observed. It was found on one hand, that if chloride was present prior to the addition of PAR, the formation of the green complex was hindered or completely prevented; while on the other hand, if the palladium-PAR complex

was formed in the absence of chloride, it could not be extracted into ethyl acetate. Therefore, it is necessary to carry out the reaction in the absence of chloride and just prior to the extraction step to add a small amount of chloride. Under these conditions, excellent results were obtained. The extractive approach has the advantage that low amounts of the palladium-PAR complex can be concentrated into a small final volume.

The green complex extracted into ethyl acetate is quite stable and has absorption maxima at 440 and 616 m $\mu$ . The molar absorptivities for these peaks are  $1.86 \times 10^4$  and  $9.5 \times 10^3$  liter/mole-cm respectively. The corresponding sensitivities are 0.0057 and 0.012  $\mu\text{g}/\text{cm}^2$ .

Further increase in sensitivity can be achieved by reextraction of the green complex into a small volume of aqueous stripping solution. In another modification, additional sensitivity can be gained by decomposing the green complex and measuring the absorbance of the free PAR which has a higher absorptivity than its palladium complex. By application of any of these modifications, it is possible to determine microgram quantities of palladium in the presence of large amounts of all metallic elements. Difficulties arise only in the presence of niobium, tantalum, silver, gold, and mercury. However, these disturbances can be overcome by an appropriate modification of the general procedure, and excellent results can be obtained for the determination of palladium.

## CHAPTER I

### INTRODUCTION

#### Historical Review

Methods based upon the absorption of electromagnetic radiation are among the most important of all the instrumental methods of analysis. Such methods have been known for many years but have gained tremendously in popularity during the last 25 years. Much of this gain in popularity has been due to the improvements in instrumentation and the availability of commercial instruments.

Monochromatic devices in the form of filters, prisms, or gratings have been available for many years. However, the greatest advances in instrumentation have come with the advent of photoelectric detectors. Prior to the development of such detectors, it was necessary to employ the human eye or a photographic plate as the detector. The errors involved in visual detection range from 5 to 20 percent because of the limited ability of the human eye to detect differences in light intensity. The application of photographic methods requires considerably more time and effort in obtaining the necessary data. With photoelectric detectors, absorbance may be read directly from a meter, or the entire spectrum may be recorded on a strip chart recorder.

One of the primary advantages of spectrophotometric analysis is that trace quantities of a substance can be determined in an easy and rapid manner. Unless extreme care is taken in the preparation of the sample, spectrophotometric methods do not yield an accuracy and precision greater

than one percent. Spectrophotometric techniques are usually applied to the determination of micro or semi-micro quantities where such accuracy and precision are commonly adequate. For macro quantities, gravimetric or volumetric methods offer greater accuracy and precision and are generally preferred.

Spectrophotometric analysis has now reached such a state of sophistication and maturity that it must be considered one of the most important methods in chemical analysis. Trace techniques, such as activation analysis, atomic absorption spectrometry, gas-liquid chromatography, and emission spectrography are gaining importance in micro analysis; however, new methods, development of new accessories and adequate low-cost equipment have maintained spectrophotometric methods at a position of prominence in the analytical laboratory.

#### Absorption of Radiation

Measurement of the fraction of the radiation that is absorbed as light is passed through the sample is the basis of spectrophotometric analysis. In general, the absorption of radiation in any spectral region results in the energy of the absorbing substance being raised from a lower energy level to a higher energy level. In the case of monoatomic atoms and ions, the only possible kind of excitation is electronic. The electrons in the lowest or ground state are raised to a higher or excited state by the energy of the absorbed radiation. The life-time of this excited state is usually quite short, of the order of magnitude of  $10^{-8}$  seconds. Thus after absorption, the substance quickly reverts to the normal ground state with concurrent release of the absorbed radiant energy.



This release may proceed by emission of light, a process called fluorescence, or the energy may be converted into thermal energy. The latter process is desirable for spectrophotometric analysis. Molecules can undergo changes in vibrational and rotational energy as well as changes in electronic energy. Because of this, molecular spectra are usually more complex than atomic spectra. The molecules that are being excited electronically by the incident radiation are not all in the same rotational and vibrational energy states. Thus a given electronic transition in a molecule which is, for example, in an excited vibrational state requires a slightly, but definitely different amount of energy from that which would be required if the molecule were in its vibrational ground state. A molecular electronic transition, therefore, is a system of relatively closely spaced lines corresponding to changes in vibrational and rotational energy superimposed on the major electronic transition.

#### Fundamental Laws of Spectrophotometry

When a beam of monochromatic radiation traverses a homogeneous layer of a substance, a portion of it is reflected, a portion is absorbed, and a portion is transmitted. Quantitative spectrophotometry is founded on the application of two fundamental laws which govern the relationship between the intensities of the light incident on, and transmitted by, an absorbing medium. The Bouguer or Lambert law states that when a parallel monochromatic beam of light passes through an absorbing medium, the intensity of the light decreases in a geometric progression as the path length is increased in arithmetic progression. This law is generally expressed in the form

$$I = I_0 10^{-k'b} \quad (1)$$

where  $I_0$  is the intensity of the incident light,  $I$  is the intensity of the light transmitted through a sample of thickness,  $b$  and  $k'$  is a proportionality constant. The second law applicable to the absorption of light is known as Beer's law, which is identical in form with equation 1, and states that the intensity of the transmitted monochromatic light decreases in a geometric progression as the concentration of the light absorbing species increases in an arithmetic progression. The law may be expressed in the form of equation 2.

$$I = I_0 10^{-k''c} \quad (2)$$

Where  $I_0$  and  $I$  designate the same quantities as in equation 1,  $c$  is the concentration of the absorbing species and  $k''$  is again a proportionality constant.

When both the path length and concentration of the absorbing species are varied, the two laws may be combined, and the resulting expression is called the Beer-Lambert law and may be expressed as

$$I = I_0 10^{-abc} \quad (3)$$

where  $a$  is the absorptivity. The equation written in this form is not convenient for the calculation of the concentration of the absorbing species. Taking the logarithms of equation 3 gives

$$\log I = \log I_0 - abc$$

and on rearrangement

$$\log \frac{I}{I_0} = -abc \quad (4)$$

If we now define  $A = -\log \frac{I}{I_0}$ , then equation 4 takes on the familiar form

$$A = abc \quad (5)$$

where A is the absorbance, b is the thickness of the absorbing sample commonly expressed in centimeters and c is the concentration of the absorbing constituent of the sample and is often expressed in grams per liter. Under these conditions, the quantity a, whose value depends on the identity of the absorbing species, the frequency of the light, the nature of the solvent, etc., is called absorptivity. If c is expressed in moles per liter, the proportionality constant is called the molar absorptivity and is given the symbol  $\epsilon$ . The terms, symbols, and definitions used in this and future chapters are those set forth by the advisory board of Analytical Chemistry (1).

### Errors in Absorption Spectrophotometry

There are several sources of error which can cause serious problems in determinations by absorption spectrophotometry. In order to facilitate the discussion of some of the more important of these errors, we will divide them into two basic groups: those that result because of solution conditions, and those that are caused by instrumental factors.

#### Solution Effects

There are several solution factors which can cause serious errors in photometric determinations. Fortunately, most of these errors are relatively easy to eliminate or compensate for by carefully controlling the solution conditions. One of the most important sources of error is due

to dissociation phenomena. Beer's law relates the absorbance of a solution to the concentration of the absorbing species. If the chemical equilibrium is shifted toward dissociation because of changes in solution volume, then the total concentration of the absorbing substance may be reduced to a greater extent than would be predicted from dilution alone, and a pronounced deviation from linearity will be observed. Dilution is not the only factor that may cause a shift in dissociation equilibrium. Changes in pH may often have a pronounced effect on such equilibria. Most of the chromogenic reagents used in developing a color for photometric analyses are also acids or bases. Changes in pH of such solutions may considerably change the degree of complexation of the solution and cause serious errors in the determination. To prevent errors from this source, most solutions are buffered at a certain pH. Changes in ionic strength may also cause variations in absorptivity; however, these deviations are usually small.

Deviations from linearity may also be caused by changes in the refractive index of the solution. Losses in light intensity due to reflection are related to the difference in the refractive indices of two media forming an interface. When mixtures of water and organic solvents are used, care should be taken to have the same ratio of organic solvent to water in the blank and in the solution to be analyzed, since otherwise the error resulting from refraction might not be entirely negligible, due to a difference in the indices of refraction of the blank and unknown.

Other solution factors that can have a pronounced effect on absorbance include the presence of colloidal or suspended solid materials (including dust) which scatter light, and thus decrease the transmitted radiant energy. Gas bubbles, dirt, and fog on the cell walls have the same

effect. The adsorption of a chromogenic substance onto the cell walls may cause errors in the absorbances measured for solutions that are examined later. The evaporation of a volatile solvent leads to a spurious increase in concentration and thus higher absorbance value. Errors may arise because of fluorescence induced by the incident radiation. Changes in absorbance may occur with time and lead to deviations. Apart from the obvious effects of temperature on equilibrium constants and concentrations, a change in temperature may result in a change in the position of an absorption band. The change in temperature alters the energy state of the absorbing species. This will have no detectable effect on the distribution between the electronic states, for these are too widely separated, but it may change the energy distribution among the vibrational modes corresponding to the lower electronic state, and thus affect both the position and the intensity of the electronic transition involved.

It is apparent that none of the examples which have been cited involves a real deviation from Beer's law. In every case the phenomena we have described would be observed even if Beer's law were rigorously obeyed by the species actually responsible for the absorption. The apparent failure of the law results from the fact that, due to the above mentioned factors, the absorbance measured is not proportional to the concentration of the species to be determined. Errors such as these are often referred to as apparent deviations of Beer's law.

#### Instrumental Errors

Beer's law is derived for the absorption of monochromatic radiation. Any instrumental factor (*i.e.*, stray light, variation in slit width, etc.) which adversely affects the monochromaticity of the light will have a

detrimental effect on the final measurement.

Non-linearity of the photodetector and meter are the most important factors in instrumental errors. An apparent deviation from Beer's law is observed if the signal obtained from the photodetector is not directly proportional to the intensity of the light striking the detector. A deviation is also observed if the meter does not respond linearly to this signal. These errors can be avoided or at least minimized by careful design of the instrument.

Variations in intensity of the light source will also cause errors. Such variations can be eliminated by employing a double-beam instrument, or can be minimized by careful regulation of the voltage applied to the light source in other instruments.

Non-reproducibility in setting the proper wavelength can cause serious errors in a spectrophotometric determination. These errors are most pronounced when the wavelength selected is on the steep portion of the absorbance curve. Care must be taken to insure that the wavelength control on an instrument is accurately adjusted and then not changed during a series of measurements. If possible, selecting a wavelength that lies on a steep portion of the absorbance curve should be avoided, and instead a wavelength that lies in the middle of a broad plateau should be chosen. This not only eliminates the errors due to inaccurately reproducing the wavelength settings, but also relaxes the requirements with respect to the monochromaticity of the light since on a plateau  $d\epsilon/d\lambda$  is zero.

In spite of the many possible sources of instrumental errors, carefully designed instruments are often capable of a greater precision than

that attained in the formation of the colored compounds. That is, deviations due to inaccuracies in weighing, volumetric measurements, instability of the colored material toward heat, light or time, and incomplete or competing reactions may cause greater deviations than instrumental errors. It is therefore important to carefully establish the conditions under which the colored compound is reproducibly formed and then to strictly adhere to this mode of operation.

#### Optimum Concentration Range in Photometric Analysis

The photometric error of an analysis is the error in the concentration which results from the instrumental error in the absorbance measurement. If we express the error in the concentration, ultimately computed from an absorbance measurement, in terms of the deviation  $\Delta C$  from the true concentration  $C$ , the relative error in  $C$  will be  $\Delta C/C$ . To relate the error in  $C$  to the error in the transmittance  $\Delta T$ , one proceeds as follows.

Beer's law may be written in the form

$$C = \frac{-(\log T)}{ab} \quad (6)$$

Differentiating this with respect to  $T$  gives

$$\frac{dC}{dT} = \frac{-0.434}{T(ab)} \quad (7)$$

Combining equations 6 and 7 gives

$$\frac{dC}{dT} = \frac{0.434C}{T(\log T)} \quad (8)$$

which on rearrangement gives the expression that allows the calculation of the relative concentration error,  $\Delta C/C$ , that depends on the photometric

error  $\Delta T$ .

$$\frac{\Delta C}{C} = \frac{0.434}{T(\log T)} \Delta T = - \frac{0.434}{T A} \Delta T \quad (9)$$

Thus the relative concentration error depends inversely on the product of the transmittance and absorbance which vary in opposite manner. Differentiating equation 9 with respect to  $T$  and setting the result equal to zero gives the point of minimum error which occurs at 36.8 percent transmittance.

Figure 1 is a plot of the ratio of the relative error in concentration per unit error in percent transmittance ( $\Delta\% T = 1$  or  $\Delta T = 0.01$ ) as a function of percent transmittance. This curve shows that in order to operate with an error close to the minimum, the sample transmittance should be within the range 20-65 percent  $T$  that is 0.2 to 0.65  $T$  (or 0.7 to 0.2 absorbance units). Consequently, variables such as the optical path length, sample size, and volume of the final solution should be adjusted in such a way so that the solutions finally subjected to the measurement show absorbance values within those limits.

#### Requirements for a Spectrophotometric Determination

In spectrophotometric methods, the quantity measured is the ratio of  $I_0$  and  $I$ . There are many commercially available instruments which can be used to obtain the required measurements. Many spectrophotometric procedures are limited by the chemical reactions upon which the procedures are based, rather than the instruments available. There are many instances where the reaction products do not possess suitable chromogenic properties. When evaluating a reagent for a spectrophotometric procedure, there are



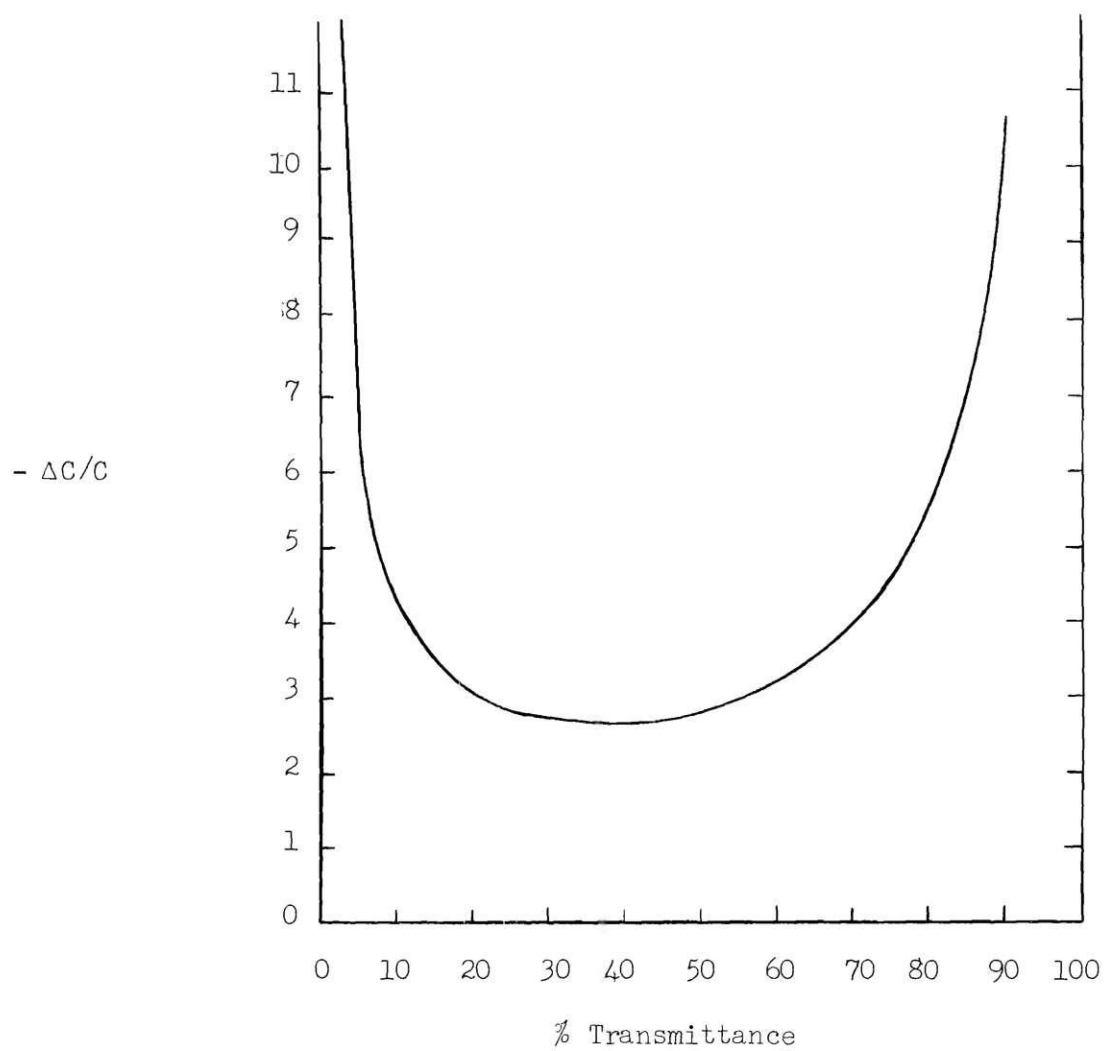


Figure 1. The Relative Error in Concentration as a Function of Percent Transmittance for Unit Photometric Error ( $\Delta \% T = 1$ ).

several points that should be considered including (a) the selectivity of the color-forming reaction, (b) the time-stability of the system, (c) the effect of excess reagent, foreign ions, pH, ionic strength and temperature, (d) conformity to Beer's law (which is desirable, but not necessary), and (e) the sensitivity of the method.

### Selectivity in Spectrophotometric Techniques

One of the most important factors is the selectivity of the chromogenic agent. Only a few reagents are specific and this is one of the major problems involved in spectrophotometric procedures. The analyst has at his disposal several possibilities that may be employed in order to improve the selectivity of a given reagent or reaction.

#### Masking

Even though many reagents per se are not selective or specific, often the reactions can be rendered selective or even specific via application of masking. The term masking is used when an undesired reaction is prevented without physically separating any species from the solution.

Masking can be accomplished by one or a combination of the following processes: (1) precipitation; (2) oxidation or reduction; (3) complexation; and (4) pH adjustment.

Masking by precipitation has several disadvantages. Besides the obvious disadvantage of causing turbidity, precipitation reactions are subject to complication by coprecipitation (via occlusion, adsorption, and other phenomena) that causes serious problems. Thus precipitation is a rather limited method for masking.

The conversion of a metal to a different oxidation state may be

used to provide a masking action. For example, iron(III) may participate in a certain reaction while iron(II) does not. Thus, if iron(III) is reduced to iron(II), the interference is prevented.

The most widely applied masking reactions are those that involve complexation. If a solution of two metals is treated with a reagent which forms a stable complex with one, while only forming a weak or no complex at all with the other, the first metal may be selectively masked from reaction with a chromogenic reagent. For example, cobalt, nickel, copper, zinc, and cadmium can be masked with cyanide and can be prevented from reaction with PAR, while lead can be determined in the presence of cyanide.

The adjustment of pH has been used to provide a masking action with certain reagents. Even though the hydrogen ion can be considered a masking reagent according to the broadest meaning of the definition, it may be argued that it should not be considered as masking the metal but rather masking the reagent and thus preventing a reaction. For example, in strongly acidic medium, EDTA does not form a complex with copper because the complex formed between the proton and EDTA is more stable than the copper-EDTA complex, thus the EDTA is masked from reacting with copper. This in no way should detract from the importance of pH adjustment in preventing an undesired reaction and for the sake of completeness in discussion is included under the term masking.

There are many reagents that have been used as masking agents. Cheng (2) has reviewed the use of masking reagents and has presented some principles which can be used for their evaluation.

When masking is not possible, one must resort to physical separations such as precipitation and filtration, solvent extraction, ion

exchange, and chromatographic techniques. If such separations are necessary, one may approach the problem from either of two positions. The desired metal may be removed alone or together with a group that will not interfere or else the bulk of interfering metals may be removed, leaving behind the metal of interest in a relatively pure form. These techniques are less desirable than masking since they require one or more additional steps in the procedure.

#### Spectrophotometric Techniques and the Noble Metals

One field that has benefited greatly from the development of photometric analysis is that of the noble metals. The number of spectrophotometric methods for the noble metals published during the last two decades probably exceeds the total number of all other reported quantitative methods for these metals. Many of these procedures involve separation techniques such as chromatography, ion-exchange and solvent extraction. These techniques are especially useful when the final determination is made by applying spectrophotometric techniques.

The method to be described in later chapters applies many of the previously mentioned techniques to enable the analyst to determine microgram quantities of palladium in the presence of large amounts of other metals.

## CHAPTER II

### THE ANALYTICAL CHEMISTRY OF THE NOBLE METALS

#### Introduction

As will be shown in Chapter III, there exists a large number of reagents and methods for the determination of palladium. A closer inspection of the situation, however, reveals that practically none of these is specific for palladium, only a few possess a certain degree of selectivity and all are subject to interference by many other metals, especially by noble metals. The application of PAR as a reagent for palladium appeared to allow the development of a method that would remedy this situation, especially with respect to interference by the platinum metals. In order to more fully appreciate and understand the difficulties to be expected and actually encountered in the development of such a method, it is desirable to examine the general analytical chemistry of the noble metals. This group includes the six platinum metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum) and gold. Because of the similarity of their physical properties and chemical behavior, separation or selective determination of the various members of the group is sometimes quite difficult. Since the platinum metals commonly occur together in nature, the analysis of ores, concentrates, and similar materials require separations unless a specific method is available. An analogous situation exists in the analysis of man-made articles such as alloys. Consequently, before undertaking a detailed discussion of the spectrophotometric methods for the analysis of palladium, it will

be useful to review such topics as the occurrence, dissolution, separation, and determination of the seven noble metals.

The material presented in the present chapter is largely based on the excellent monograph by Beamish (3) and the chapter on noble metals by Walsh and Hausman (4) in The Treatise on Analytical Chemistry edited by Kolthoff and Elving. Some effort has been made to incorporate the relevant papers that have appeared recently and are not covered in these two publications.

#### The Occurrence of the Noble Metals

The six platinum metals occur predominantly in nature as the native metals; however, rarely in a pure state, but more commonly alloyed with one or more members of the family and to a lesser extent with iron, nickel, copper, chromium, and gold. The platinum metals have an approximate distribution in the earth's crust as follows (5):

<u>Metal</u>	<u>Percent</u>
Platinum	$8.0 \times 10^{-11}$
Iridium	$3.0 \times 10^{-12}$
Osmium	$6.0 \times 10^{-12}$
Palladium	$8.5 \times 10^{-13}$
Rhodium	$9.0 \times 10^{-13}$
Ruthenium	$2.3 \times 10^{-13}$

Very few of the platinum metals occur as minerals, of which, cooperite, PtS; braggite, (Pt, Pd, Ni)S; laurite, RuS<sub>2</sub> or (Ru,Os)S<sub>2</sub>; potarite, PdHg; sperrylite, PtAs<sub>2</sub>; and stibiopalladinite, Pd<sub>3</sub>Sb are the most important.

Several of the native alloys have received special names such as platinum-iridium, iridosime, and osmiridium. Gold often occurs alloyed with the platinum metals as well as in the metallic state. The noble metals are mainly found in southern Europe, western United States, Canada, Brazil, South Africa, and Central Asia.

### Dissolution of the Noble Metals

#### Ruthenium

The metal is insoluble in mineral acids, even in aqua regia. Ruthenium metal, its oxides and insoluble salts are readily attacked by fusion with sodium peroxide or oxidizing mixtures of alkali or alkaline earth compounds.

#### Osmium

Osmium is a very hard and infusible metal and is not attacked by acids unless they are oxidizing agents. When fused with sodium peroxide or potassium nitrate and potassium hydroxide, the metal is converted to water soluble osmate,  $K_2OsO_4$ .

#### Rhodium

Rhodium in the form of massive or powdered metal resists attack by aqua regia and all single mineral acids except sulfuric acid. The latter will attack powdered rhodium at elevated temperatures. The metal is also attacked when fused with alkali or alkaline earth bisulfates or hydroxides, and is soluble in molten lead.

#### Iridium

This metal is exceedingly resistant to attack by any mineral acid, single or mixed. When fused with alkali or alkaline earth hydroxides or

nitrates, or sodium peroxide, the metal is converted to an acid-soluble compound.

#### Palladium

Palladium is more readily attacked by various reagents than any other member of the family. It readily reacts with nitric and sulfuric acids and especially with aqua regia. It resists hydrochloric acid in the absence of oxidizing agents. The metal is readily attacked by fusion with alkali or alkaline earth hydroxides or peroxides.

#### Platinum

The massive metal is inert to all single mineral acids, but it is dissolved by aqua regia. When in powdered form, it is at least partially dissolved by hot concentrated sulfuric acid. Although platinum may be attacked by fusion with alkali hydroxides and peroxides, the metal is not completely dissolved.

#### Gold

The metal is not attacked by any of the mineral acids, but is readily soluble in aqua regia. Fusion with sodium hydroxide produces a difficultly soluble product, while fusion with potassium hydroxide produces the readily soluble potassium aurate.

If a solution containing the noble metals is subjected to a reductive treatment, the precipitated metals can be dissolved in the following manner. Platinum or gold will dissolve in aqua regia; palladium, in aqua regia or hot sulfuric acid; rhodium will dissolve in hot concentrated sulfuric acid; iridium, ruthenium or osmium will dissolve in none of the above mentioned acids. The most general method for bringing the group of platinum metals into solution is fusion with a mixture of barium



peroxide and barium nitrate and dissolving the melt in dilute hydrochloric acid.

### Methods of Separation of the Noble Metals

#### Osmium and Ruthenium

The usual method for separating these metals from each other and from the other noble metals is based on the fact that they both form volatile tetroxides. For the simultaneous removal of both metals, one may use an oxidation with a variety of reagents such as sodium bromate, perchloric acid, or in caustic media, chlorine. The tetroxides may be trapped in 10 percent sodium hydroxide solution. For the separation of osmium from ruthenium one can selectively oxidize osmium with either nitric acid or hydrogen peroxide and trap the distilled osmium tetroxide in a solution of hydrogen peroxide. After removal of osmium in this manner, ruthenium is distilled as the tetroxide as it is formed by oxidation in a sodium bromate-sulfuric acid mixture. Separations based on tetroxide formation are not as simple as they may appear. Problems are encountered if chloride is present since the chloro-complexes of osmium and ruthenium are particularly resistant to the quantitative formation of the tetroxide. Even so this approach is generally taken when separations are required.

#### Gold, Platinum, and Palladium

Practically all of the conventional methods for separating the noble metals involve the separation of osmium and ruthenium as tetroxides followed by the precipitation of gold, platinum, and palladium. Several possibilities are available for the separation of these latter three

metals. Gold can be precipitated by selective reduction with hydroquinone. Sulfur dioxide, sodium nitrite, and oxalic acid have also been proposed for reducing gold, but none is as selective as hydroquinone. The latter reagent offers the additional advantage that after the removal of gold, palladium may be precipitated with dimethylglyoxime directly in the filtrate from the gold precipitate. The determination of platinum usually follows the separation of gold and palladium. One of the oldest reagents for the precipitation of platinum is ammonium chloride. Zinc has been used as a reducing agent to precipitate platinum as the metal. Another such reagent is tin(II) chloride. With the latter reagent tellurium is used as the scavenger.

Solvent extraction techniques have been applied to the separation of gold, platinum, and palladium. For gold the most effective solvent extraction is that of bromoauric acid with isopropyl ether (6). A single extraction removes 98-100 percent of the gold from solutions containing 0.1 mg gold per 10 ml. The dimethylglyoxime-palladium complex can be extracted with chloroform (7). Only a few extractive methods have been reported that are selective for platinum.

#### Rhodium and Iridium

These two metals are commonly isolated simultaneously from the other noble metals. They are both resistant to the usual acids, but dissolution can be achieved by fusion with alkali or alkaline earth peroxide and treating the melt with dilute nitric acid. The separation of rhodium from iridium is the most difficult of all noble metal separations. The most effective method is to selectively reduce rhodium with metallic copper. In fire assay techniques rhodium and iridium constitute most of

the so-called insolubles.

### Fire Assay Techniques

Fire assay techniques are by far the most common methods of concentration, and separation of the noble metals from the common base metals. These techniques involve the collection of the noble metals in a lead button. Initially the ore to be analyzed must be ground to a very fine powder. The sample is then mixed with a flux of sodium carbonate, lead oxide, borax and flour or carbon, and heated in a high temperature furnace. Sodium carbonate and borax react with the sample forming complexes, thus exposing the noble metals to the extractive action of the lead formed when lead oxide is reduced by the reaction with flour or carbon. During the fusion process the lead, because of its higher density, settles toward the bottom of the pot and alloys with the noble metals. In order to facilitate the alloying, frequently silver is added to the fusion mixture. The next step in the process is called cupellation and achieves a separation of the noble metals and silver (present in the ore or added to the fusion mixture) from lead. Cupellation is carried out in a vessel known as the cupel which is commonly made from bone ash. Under suitable conditions of temperature and exposure to air, the lead in the cupel is oxidized to form lead oxide, which is liquid at the prevailing temperature. The lead oxide is absorbed by the bone ash and carries with it such base metals as copper and nickel. About 98 percent of the lead oxide is absorbed and the remainder is volatilized, leaving a silver bead containing the noble metals. The silver bead may now be dissolved in nitric or sulfuric acid.

Ruthenium and osmium usually are subject to serious losses during

fire assay and cupellation. Rhodium is one of the most well behaved of the platinum metals so far as lead collection is concerned. Iridium does not alloy with lead but is collected as a suspension in the lead button. The classical fire assay for gold, platinum and palladium is one of the most effective methods for their concentration and separation from base metals.

### Determination of the Noble Metals (3)

#### Ruthenium

There are no reagents that are specific for the gravimetric determination of ruthenium. This shortcoming is somewhat compensated by the ease with which ruthenium may be separated from interfering ions by distillation. Ruthenium may be precipitated in the classical manner with hydrogen sulfide, zinc, magnesium, ethanol, etc.

In all instances the weighing form is the metal and to obtain it involves heating in air, followed by reduction in hydrogen and cooling in carbon dioxide. There are several non-selective organic sulfur compounds that can be used to precipitate ruthenium from the tetroxide distillate. Of these, thionalide (8) is probably the most useful.

Only a few titrimetric procedures have been reported for ruthenium; all of them require a prior separation and their reliability is low. The best method is that of Howe (9) which involved the reduction of ruthenium(IV) with an excess of tin(II) chloride and back-titration with iodine. But even this method gives results that are three to twelve percent low and it is recommended only for an approximate determination.

The most sensitive method yet recorded for ruthenium is a catalytic

procedure (10) which utilizes a spectrophotometric measurement. This approach involves ascertaining the quantitative relationship between the concentration of ruthenium and the time required to catalyze the oxidation of arsenic(III) by cerium(IV). Other reagents that have been proposed for the spectrophotometric determination of ruthenium include 1,10-phenanthroline (11), acetylacetone (12), 1,4-diphenylthiosemicarbazide (13), sodium thiocyanate (14), thiourea (15), and anthranilic acid (16).

### Osmium

There are no reliable gravimetric procedures for the direct determination of osmium in ores. The usual approach is to isolate osmium by distillation of the tetroxide and for such distillates there are several gravimetric methods available. Various standard reducing agents such as aluminum, hydrazine and formaldehyde have been applied but often give erroneous results. The most effective gravimetric methods involve precipitation by sodium bicarbonate (17), strychnine sulfate (18), thionalide (8), acridine (19), and 2-phenylbenzathiazole (20). Most of these require the metal as the final weighing form, and ignition followed by reduction in hydrogen is necessary.

A number of titrimetric methods have been described for the determination of osmium. Most of these methods require rather tedious techniques to minimize the loss of volatile constituents or to prevent air oxidation of sensitive reagents. Hydrazine sulfate (21), titanium(III) chloride (22), chromium(II) sulfate (23), and iron(II) sulfate (24) have been used as titrants for the potentiometric titration of osmium.

Spectrophotometric methods are especially useful for osmium because the metal is commonly encountered as a minor constituent in the

sample. There are no methods available for the direct determination of osmium in the presence of the other platinum metals, but its isolation as the tetroxide is usually easy after selective oxidation with nitric acid or hydrogen peroxide. The following reagents have been used for the determination of osmium: 1,4,6,8-naphthylamino trisulfonic acid (25), anthranilic acid (26), and thiourea (27). The most sensitive methods that have been developed are catalytic (28). These procedures involve photometric methods to determine the increase in the rate of various redox reactions caused by increasing amounts of osmium.

#### Rhodium

Rhodium is a very minor constituent in platinum metal ores and its analytical isolation has long been a problem. The metal resists attack by the usual acids and oxidizing mixtures, but it is dissolved under suitable conditions by sulfuric acid and by fusion with certain acid sulfate salts. Only a few analytical methods for the determination of rhodium exist. No gravimetric reagent is specific and prior separation of ruthenium is necessary. Selective corrosion by treatment with various acids, acid salts, and oxidizing mixtures has, until recently, been the only method available. Such procedures require considerable time and are often inaccurate. The most difficult separation is that of rhodium from iridium. An accurate separation of  $\mu\text{g}$  amounts of rhodium from iridium has been effected by selective reduction with powdered antimony (29). In addition, such techniques as chromatography, ion-exchange, and solvent extraction have been applied to achieve this separation. The following reagents have been proposed for the gravimetric determination of rhodium: thiobarbituric acid (30), 2-mercaptobenzoxazole (31),

thioacetamide (32) and hydrogen sulfide (33). In most cases reduction to the metal is required for the final weighing.

There are few reliable titrimetric procedures for the determination of rhodium. The titration of rhodium(V) with iron(II) sulfate has been reported (34) and is useful for the routine determination of isolated rhodium. Thionalide (35) and sodium-1-piperidine carbodithioate (36) have also been reported as titrimetric reagents for rhodium.

Rhodium is usually found in relatively small proportions in deposits of platinum metals and because of this, spectrophotometric methods are most useful in their analysis. One of the best spectrophotometric determinations of rhodium employs tin(II) chloride (37). This reagent is especially useful since about 20 times as much iridium as rhodium can be tolerated. A 1:1 mixture of 1,4-diphenylcarbazide and 1,4-diphenylcarbazone (38) is a very sensitive reagent for the determination of rhodium. Thiomalic acid (39), 1-nitroso-2-naphthol (40), 2-mercapto-4,5-dimethylthiazole (41) and 5-amino-2-mercaptobenzimidazole (42) have all been proposed as reagents for rhodium.

### Iridium

The same difficulties that are encountered in the determination of rhodium apply to iridium. Iridium is inert to all mineral acids unless it is very finely divided, and fusion with alkali peroxide is usually required to open iridium alloys. There are a few reliable gravimetric methods but none of them is specific. Those that are worthy of mention employ 2-mercaptobenzothiazole (43), thiourea (32), p-aminophenyl-dithiocarbonate (44) or tetraphenylarsonium chloride (45). With the exception of the last reagent none of the precipitants produce compounds

that can be used as a weighing form and ignition followed by reduction with hydrogen is usually required.

Several titrimetric methods have been reported for the determination of iridium; all of these are based on oxidation or reduction between the tri- and quadrivalent states. Most of these methods apply potentiometric endpoints and the results are usually inaccurate. Many base and platinum metals interfere, necessitating a prior separation of iridium.

Only a few spectrophotometric methods have been described for iridium, and commonly require a close control of the composition of the medium in which the color is developed. One of the most sensitive reagents for iridium is leuco crystal violet (46) which allows the determination of 0.5 to 4 ppm iridium. This method is relatively free from interferences by associated platinum metals and certain base metals. Another quite sensitive procedure utilizes tin(II) bromide as the reagent (47). The main disadvantage of this method is that it suffers from excessive interferences and usually a preliminary separation of iridium is necessary. Tetraphenylphosphonium bromide (48), EDTA (49) as well as a mixture of perchloric and phosphoric acids (50) have been proposed as photometric reagents for iridium.

### Platinum

There are only a few gravimetric methods for platinum and none of them is specific. Of the few methods available the most commonly employed is the precipitation with ammonium chloride (51). Only a few base metals interfere and among the platinum metals iridium, rhodium, and palladium interfere to some degree. The most serious objection to this method is the appreciable solubility of the ammonium hexachloro-



platinate(IV). Other reagents that have been proposed as gravimetric reagents for platinum are tetraphenylarsonium bromide (52), and phenylthiosemicarbazide (53).

Very few titrimetric methods have been recorded, and none is recommended for other than the most restricted application. Since reliable results are usually obtained only with pure platinum solutions, these techniques have little value.

A number of spectrophotometric methods have been proposed for the determination of platinum and they offer the most acceptable approach. One of the best reagents is tin(II) chloride (54). The color develops rapidly and is quite stable. Another reagent that is useful for this purpose is p-nitrosodimethylaniline (55). This reagent is useful over the range of 0.7 to 2.4 ppm platinum. Its main disadvantage is that more than one colored species can form, thus necessitating strict adherence to the prescribed procedure. Other reagents that have been proposed are potassium iodide (56), o-phenylenediamine (57) and anthranilic acid (58).

#### Palladium

A large number of excellent gravimetric procedures for the determination of palladium are known and new ones appear regularly in addition to modifications of the older ones. Methods for the determination of palladium are more numerous than for any of the other platinum metals. To seek the most suitable gravimetric reagent for palladium can be a frustrating experience. Beamish (3) lists 50 different reagents that have been used for the analysis of palladium. The most important group of reagents for the precipitation of palladium is the oxime family of which dimethylglyoxime is the member most commonly used. The first

applications of dimethylglyoxime were recorded by Duparc (59). Since its introduction as a precipitant for palladium, the method has undergone many modifications. Basically the precipitation is carried out in a dilute hydrochloric acid solution and the yellow precipitate is filtered, dried at  $110^{\circ}\text{C}$ , and weighed. Of the associated platinum metals only gold and platinum interfere. Another reagent that has often been used for precipitation of palladium is potassium iodide (60). The method is not as selective as the preceding one but is quicker and at least as accurate. The precipitate is very stable, filters readily, and can be easily reduced to the metal; however, the procedure is subject to interference by many metals. Another approach is reduction to palladium metal, and this is often used when the sample contains relatively few foreign constituents. Formic acid is an excellent reagent for the reduction of palladium (61). For a more complete review of the gravimetric methods for palladium the reader is referred to Beamish's review (3).

More than a dozen methods have been proposed for the titrimetric analysis of palladium. Many of these involve the formation of insoluble palladium compounds and employ instrumental endpoint detection. None of these methods can be applied to samples containing mixtures of the platinum metals. There are a variety of indirect titrations that have been proposed for the determination of palladium and most of these involve the use of EDTA. Flaschka (62) developed a method involving the addition of an excess of a potassium tetracyanonickelate(II) solution to the palladium solution. This results in an exchange of metal ions, thus releasing a stoichiometric amount of nickel. The latter is titrated in an ammoniacal medium with EDTA using murexide as the indicator. Several titrations

have been proposed in which an excess of EDTA is added and a back titration with an appropriate metal is applied (63).

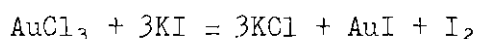
There are more than one hundred recorded methods for the spectrophotometric determination of palladium. Since the present investigation involves a spectrophotometric method, an extensive discussion of these procedures is deferred until Chapter III.

### Gold

A number of methods have been developed for the gravimetric determination of gold. Most of these methods involve reduction to the metal which is quite readily accomplished. Oxalic acid (64) is one of the most frequently used reductants for gold. The reagent has the following advantages: it is stable, readily obtained in a pure state, and excess reagent does not interfere in later operations. Another effective reductant for gold is hydroquinone (65). With this method there are less interferences from platinum and palladium, and the latter can be easily determined by precipitation with dimethylglyoxime in the filtrate from gold. Inorganic reductants such as sulfur dioxide, iron(II) sulfate and sodium nitrite have been used but lack selectivity. A few reagents produce organic weighing forms with the advantages of easy transfer, purification, and favorable weighing factors. The following reagents have been used for this purpose: thiophenol (66), and thioglycollic acid (67).

Titrimetric methods for the determination of gold usually require a precipitation of the metal or the gold(I) salt. In most these, the endpoints are determined by potentiometric techniques or by back titrating the excess reductant. Among the most suitable reductants for

titrations of gold are hydroquinone (68), iron(II) sulfate (69), and ascorbic acid (70). Potassium iodide is a notable exception to the general type of reductant involved in gold titrations. In this method (71) potassium iodide is added to a solution of gold(III) at pH 5 in amounts enough to redissolve the gold(I) iodide first precipitated. The reaction is commonly written as



The liberated iodine is titrated with standard thiosulfate to a starch endpoint.

The acceptable methods for the spectrophotometric determination of gold usually require some degree of isolation of the metal. Such methods as fire assay, solvent extraction, chromatography, and selective precipitations have been used for this purpose. Most spectrophotometric methods for gold involve the absorbance measurements on colloidal gold solutions, or on the colored oxidized products of the organic precipitants, or on an organic extract of the colloidal suspension. Organic reagents that have been proposed include: o-tolidine (72), rhodamine B (73) and dithizone (74). The bromaurate method by McBryde and Yoe (6) involves the absorbance measurement of the orange bromaurate(III).

## CHAPTER III

## SPECTROPHOTOMETRIC METHODS FOR PALLADIUM

Introduction

Many methods have been proposed for the spectrophotometric determination of palladium. The literature prior to 1963 is reviewed by Beamish in a series of papers (75,76,77), and in his book The Analytical Chemistry of the Noble Metals (3). These reviews list over 65 different reagents that have been proposed for the determination of palladium, many of which have been applied in more than one procedure. Since 1963, an additional 35 to 40 reagents have been suggested for the spectrophotometric determination of palladium. Thus, more than one hundred procedures have been published to date. With such an abundance of reagents and methods available, the task of selecting the most suitable procedure for a particular case becomes quite difficult.

One may well question the need in developing still another method when there are so many already available. However, a critical examination reveals considerable shortcomings with most of the existing methods and thus further investigation can still be justified. Of the over one hundred methods that have been proposed for the determination of palladium only about one tenth have a certain degree of selectivity. Many of the reagents studied are extremely sensitive for palladium; however, they also react in a similar manner with many of the other metals that commonly accompany this element, including the other platinum metals, iron,

copper, chromium, or gold. Therefore, a useful method should be relatively free from interference by at least these metals.

#### Review of Spectrophotometric Methods

Not only is the problem of selecting a procedure for the determination of palladium difficult, but it is also a rather formidable task to simply review the merits of the various procedures that have been proposed. In an attempt to simplify this undertaking while still maintaining the purpose of this chapter, that is, to review the pertinent methods for the spectrophotometric determination of palladium, the following approach will be taken. The procedures that have appeared in the literature since 1963 are compiled in a tabular form so that the reader may easily compare the various methods. Next, the more important procedures which were developed prior to 1963 will be discussed. The reader who is interested in a more complete review of these earlier methods is referred to the previously mentioned publications and the book by Beamish.

#### Methods Appearing After 1963

Table 1 is a compilation of the methods that have appeared in the literature since the publication of the last review by Beamish (77). This table lists the range of concentration over which the method is applicable, the wavelength of maximum absorbance, some pertinent procedural details, and finally the metals that were reported to cause interference. In all cases only a few interferences are mentioned; however, that does not imply that non-listed metals do not interfere. Commonly the metals listed are the only ones that the author has included in his study. An examination of this table reveals that only a few of the listed

Table 1. Recent Spectrophotometric Methods for the Determination of Palladium

Reagent	Range of Conc. in ppm	Interferences	Comments	Ref.
1	0.4-6.0	Au, Pt, Cu, Ag, Th, Mg, Cr, U, V, (Ir, Os, Ru, Rh, > 2:1)	380 m $\mu$ , pH 3-6.5	(78)
2	1.0-25.0	Au, Pt	372 m $\mu$ , 3 F HAc stable 15 hrs.	(79)
3	8.0-32.0	Pt. Metals, Fe, Co, Ni	635 m $\mu$ , 1.5-2.1 F HCl 30 min. standing. Stable 90 min.	(80)
4	2.5-39.3	Pt > 240:1	496 m $\mu$	(81)
5	0.4-3.0	Pt, Os, Fe, Co, Ni	540 m $\mu$ , stable several hours	(82)
6	1.0-8.0	Pt, Pt. metals > 10 ppm	400 m $\mu$ , 40 min. standing	(83)
7	0.02-2.0	Ru, Ir, Rh, Pt	310 m $\mu$ , pH 2.1- 3.0	(84)
8	0.4-25.0	Zr, Hf, Fe, Co, Th, U, Sc, La, Ti	green filter pH 3.5	(85)
9	0.2-10.0	Pt metals do not	405 m $\mu$ , 2-3 F HCl extn. CHCl <sub>3</sub>	(86)
10	1.0-15.0	Au	533 m $\mu$ , pH 2-3	(87)
11	0.4-10.5	not reported	420 m $\mu$ , pH 1-11	(88)
12	0.1-10.0	not reported	408 m $\mu$ , 10 F HClO <sub>4</sub>	(89)
13	-----	Au, Pt, Ag, Fe	570 m $\mu$ , pH 2-4 extn. benzyl alc.	(90)
14	0.5-10.0	Os, Cu, Fe, Pt	320 m $\mu$ , pH 2-2.5 extn. CHCl <sub>3</sub>	(91)

Table 1. Continued

Reagent	Range of Conc. in ppm	Interferences	Comments	Ref.
15	4.0-98.0	not reported	610 mμ, pH 4.6-5.6	(92)
16	1.0-7.3	Pt, Ag, Pb, Al	315 mμ, pH 4.6-7.3 extn. BuOH, back extn. H <sub>2</sub> O	(93)
17	0.8-9.8	Pt, Au, Hg, Ni	574, 619 mμ, pH 4.2-4.5	(94)
18	0.0-10.0	Hg, Ag	520 mμ, pH 3 ± 0.2 50:50 EtOH EDTA for masking	(95)
19	0.4-20.0	Ce, Ag, Pt	546 mμ, pH 4.5-6.0, 80% dioxane, heat 60-65° for 20 min.	(96)
20	0.5-12.0	Pt >400:1	pH 6.2-6.8	(97)
21	0.3-8.0	>200:1 Pt, Ru, Rh, Ir, Os, Fe, Ni, Co, Zn, Cu	406 mμ, 0.25-2.8 <u>F</u> H <sub>2</sub> SO <sub>4</sub> extn. CHCl <sub>3</sub>	(98)
22	0.6-6.0	Sn, Mn, Co	430 mμ, pH 4 stable 72 hrs.	(99)
23	1.5-7.0	>100:1 Pt, Ir, Rh Au, Co, Ni, Fe	594 mμ, pH 1.5-2.3 must fume with H <sub>2</sub> SO <sub>4</sub> , unstable in light	(100)
24	0.5-7.0	Rh, Pt, (>50:1 Os, Ru, Ir)	410 mμ, 1.5-1.55 <u>F</u> HCl	(101)
25	0.05-0.5	not reported	428 mμ, pH 2.0	(102)
26	0.02-0.1	Pt, Ir, Au	397 mμ, pH 1 requires 5 extns.	(103)



Table 1. Continued

Reagent	Range of Conc. in ppm	Interference	Comments	Ref.
27	0.8-9.6	not reported	520 m $\mu$ , pH 11.5- 11.8 stable for 30 min.	(104)
28	-----	Au, Ag, Hg, Pt	436 m $\mu$ , pH 1.5 heat 100° for 15 min. extn. CHCl <sub>3</sub>	(105)
29	0-10.0	Pt does not	436 m $\mu$ , extn. CHCl <sub>3</sub>	(106)
30	-----	Pt does not	317 m $\mu$ , pH 1-4 extn. CH <sub>2</sub> Cl <sub>2</sub>	(107)
31	-----	Fe, Mo	505 m $\mu$ , dil. HCl extn. CHCl <sub>3</sub>	(108)
32	0.2-2.0	Pt metals do not	440, 630 m $\mu$ , 0.05- 5 F H <sub>2</sub> SO <sub>4</sub> extn. ethyl acetate	(109)
33	-----	Require prior separation	452 m $\mu$ , 2 F HCl extn. CHCl <sub>3</sub>	(110)
34	20-100	Pt, Ir, Au, Fe, Zn, Ni, V, Cu, Bi, Mn, Cd, Hg if >100:1	397 m $\mu$ , pH 1 HCl- KCl-EDTA used for masking, extn. CHCl <sub>3</sub>	(111)

Key to Reagents for Table 1

- (1) 2-Mercaptobenzothiazole
- (2) 1-Phenylthiosemicarbazide
- (3) Tin(II) chloride
- (4) Tropaeolin OO
- (5) Quinoxaline-2,3-dithiol in N,N-dimethylformamide
- (6) 5-Amino-2-benzimidazolethiol

- (7) Potassium thiocyanate
- (8) o-(2)Hydroxy-3,6-disulfo-1-naphthylazo)benzene arsonic acid
- (9) 1-Mercaptopropionic-p-phenetidide
- (10) Chrysoidine
- (11) Nitroso-R salt (Sodium 1-nitroso-2-naphthol-3,6-disulfonate)
- (12) Potassium iodide
- (13) Phenoselanazine
- (14) Potassium thiocyanate and tetraphenylarsonium chloride
- (15) 5-(3-Methyl-5-oxo-1-phenyl-2-pyrazoline-4-yl)salicyclic acid
- (16) Sodium azide
- (17) Phenosafranine
- (18) 4,4'-bis(Dimethylamino)thiobenzophenone
- (19) 2-Hydroxyazobenzene
- (20) Sodium( $\alpha$ -naphthylamino)azobenzene-p-sulfonate
- (21)  $\beta$ -Mercapto- $\beta$ -phenylpropiophenone
- (22) 2-Thenoyltrifluoroacetone
- (23) Pyridine-2-aldehyde-2-quinolyhydrazone
- (24) Tin(II) chloride (tri-n-octylamine solvent)
- (25) Disodium-1-amino-8-hydroxynaphthalene-3,6-disulfonate
- (26) Glyoxime
- (27) Pyridine-2-aldehyde-2-pyridylhydrazone
- (28) Diethyldithiocarbamate
- (29) Oxime
- (30) Phenylacetylene
- (31) Thioxine (8-mercaptoquinoline)
- (32) 4(2-Pyridylazo)resorcinol
- (33) Dithizone
- (34) Glyoxime

methods are free from interference by other platinum and base metals. The more promising of these reagents will be discussed in some detail in the following paragraphs.

The procedure described by Sangal and Dey which utilizes o-(2-hydroxy-3,6-disulfo-1-naphthylazo)benzene arsonic acid (85) seems to be free from interference by other platinum metals. This work was carried out using a filter photometer with a green filter (transmission 520-580 m $\mu$ ). Beer's law is obeyed over a sufficiently wide range and the color is stable for at least 30 minutes. Although a number of metal ions cause interference, none was reported for platinum(IV), silver, gold, copper, cobalt or chromium(VI).

1-Mercaptopropionic-p-phenetide (86) has been applied in an extractive determination for palladium. Other platinum metals in concentrations as high as 1000 times that of palladium do not cause an interference.

4,4'-bis(Dimethylamino)thiobenzophenone (95) is a sensitive reagent for the determination of palladium. The reaction is carried out in a 50:50 ethyl alcohol-water mixture from which the complex can be extracted into iso-amyl alcohol. The reagent forms colored complexes also with other platinum metals, but they are not extracted. However, mercury and silver interfere.

The extractive method developed by Ziegler and Buchholz (107) is free from interference from other platinum metals present up to a 1000 fold excess. In this procedure the palladium is extracted from an acidic aqueous medium by shaking with a solution of phenylacetylene in dichloromethane; the absorbance is measured at 317 m $\mu$ .

Busev and Ivanov (109) proposed the use of 4-(2-pyridylazo)resorcinol (PAR) as a reagent for the spectrophotometric determination of palladium. They reported the formation of two complexes, one in neutral medium and the other in strongly acidic solution. They erroneously reported that the complex formed at pH 7 is unstable and recommended the use of the complex formed in strong sulfuric acid solution. The green palladium-PAR complex formed in acidic medium is extractable into ethyl acetate. They reported adherence to Beer's law over the range 0.2-2.0 ppm. Other platinum metals as well as many other metals do not interfere.

The method proposed by Marczenko and Krasijko (110) requires a prior separation of palladium by precipitation with dimethylglyoxime, nickel being used as a scavenger. The mixed precipitate is suspended in 2 F hydrochloric acid and extracted with a chloroform solution of dithizone.

#### Methods Prior to 1963

In this section only those procedures that are relatively free from interference by associated platinum or base metals will be discussed.

Gustin and Sweet (112) described a procedure utilizing 8-aminoquinoline as the reagent. The method is useful over the range 2 to 150  $\mu\text{g}$  palladium per 50 ml of solution. The reaction with palladium(II) is carried out in a solution adjusted to pH 2.5 or less. A yellow insoluble chloride-containing complex is formed that converts to an insoluble violet complex at pH 10.2. The latter compound is readily extracted into chloroform and the absorbance may be measured at 590  $\text{m}\mu$  within one hour after extraction. The results obtained indicated appreciable freedom

from interference by copper, iron, chromium(III), nickel, and platinum metals (with the exception of iridium which interferes even if present in relatively small proportions).

One of the most effective methods for determining traces of palladium in the presence of many of the base metals frequently associated in such natural occurrences as ores, concentrates or alloys, involves the selective isolation of palladium by coprecipitation with tellurium after reduction by tin(II) chloride (113). The procedure calls for the simultaneous reduction of palladium and tellurium in 3 F hydrochloric acid. The mixed precipitate is redissolved, p-nitrosodiphenylamine added, and the palladium complex formed is extracted into diethyl-oxalate. Gold and silver are also reduced by tin(II) and must be absent; however, up to 100  $\mu$ g of each of the other platinum metals as well as of iron, copper, nickel, cobalt, lead and chromium can be tolerated. The range of palladium concentration is given as 0.2 to 1 ppm.

Busev and Naku (114) introduced l-mercaptopropionic-p-anisidide for the determination of palladium. The reagent forms a yellow complex that has a mole ratio of palladium to reagent of 1:2. The complex is readily extractable into chloroform or benzene from a medium 0.1-3.0 F in hydrochloric acid; the maximum absorbance is at 410  $m\mu$  in either solvent. Approximately 30 minutes is required for complete color development. Beer's law is obeyed over the range 0.2-12 ppm. No interference from platinum(IV), rhodium(III), iridium(IV), or osmium(IV) is reported for proportions as high as 1000:1 metal to palladium. Copper is the only metal that appears to be a serious interference.

Didodecyldithio-oxamide (115) has been applied as a reagent for

the determination of palladium in solutions about 7.5  $\text{F}$  in hydrochloric acid. The optimum concentration range is 1-4 ppm palladium. The color requires about 15 minutes to develop and is stable for at least 48 hours. The method has proved useful for the determination of palladium in the presence of 160 times as much platinum(IV). Osmium and iridium do not interfere, but gold does. No reference was made to interferences by any other metals.

The spectrophotometric determination of palladium employing the sodium salt of 1-nitroso-2-naphthol-3,6-disulfonate (Nitroso-R salt) (116) allows for analysis in the range 1.3 to 4.3 ppm. The red complex is water soluble and no extraction is required. The maximum absorbance occurs at 430  $\text{m}\mu$ , but at this wavelength the reagent absorbs significantly and the plateau at 500-510  $\text{m}\mu$  is more suitable for the measurement. No interference is caused by platinum, rhodium, osmium, or gold in concentrations 20 to 40 times that of palladium.

Phenyl-1-pyridyl ketoxime (117) is a useful reagent for the spectrophotometric determination of palladium. This compound forms a yellow precipitate containing 1 mole palladium to 2 moles of ketoxime. The compound is extractable into chloroform and has absorbance peaks at 410 and 340  $\text{m}\mu$ . Beer's law applies over the range 0.5-14 ppm palladium. Since there is some absorption by the reagent at 340  $\text{m}\mu$ , the maximum at 410  $\text{m}\mu$  is recommended. The most favorable acidity for the formation and extraction of the palladium chelate is pH 8.5-10. The reagent forms colored complexes with iron(II), cobalt, nickel, and copper that are also extractable. However, these interferences can be avoided by the addition of EDTA which has no influence if the absorbance is measured at 410  $\text{m}\mu$ .

When operating at 340 m $\mu$ , EDTA must be included in the blank. Of the noble metals, only gold interferes.

Thionalide (118) has been used for the determination of palladium. The complex is extracted from 2-3 F hydrochloric acid into a 2:1 chloroform-isoamyl alcohol mixture. The absorbance is measured at 375 m $\mu$ , 10-15 minutes after the extraction. Beer's law is obeyed over the range of 0.4-12 ppm. Palladium can be determined in the presence of 1000 times its amount of platinum, rhodium, iridium, osmium, cobalt, and nickel. Tartaric acid is used to mask molybdate, iron(III), bismuth, zinc, lead and tin(IV). An accuracy of  $\pm 5$  percent is claimed.

1-Nitroso-2-naphthol (119) has been used for the spectrophotometric determination of palladium. The orange-colored complex can be extracted from a weakly acidic solution into toluene. Any excess reagent is also extracted and must be removed by stripping the organic phase with a sodium hydroxide solution. The maximum absorbance is at 420 m $\mu$  and Beer's law is obeyed over the range 0.5-5 ppm. The method is relatively free from interference by other platinum metals, but copper, nickel, cobalt, chromium and iron interfere.

#### Evaluation of Existing Methods

An inspection of the methods discussed in the foregoing sections allows the following summarization. There are several methods which combine high sensitivity with simplicity of procedural detail. However, selectivity and freedom of interference often leave much to be desired. On the other hand, methods relatively free from interferences are usually lacking in sensitivity and often require very tedious procedural details.

While it is true that probably for every particular composition of sample an adequate method can be selected from the array of proposed procedures, if one includes a preseparation when necessary, the challenge to develop an ideal method still exists. Such a method should allow for the determination of palladium within a matrix containing any or all of the other elements, should possess the desired level of sensitivity and should involve a procedure as simple as possible. PAR appears to be the reagent most suitable for developing such a method. To what degree this ideal has been approached will be shown in Chapters VI and VII of this thesis.



## CHAPTER IV

### THE ANALYTICAL APPLICATION OF 4-(2-PYRIDYLAZO)RESORCINOL (PAR)

#### Historical Review

Pyridine-azo compounds with a hydroxyl group in the ortho-position to the azo group form a very promising class of analytical reagents, particularly in the field of metallochromic indicators. Compounds of this class were first synthesized in 1918 by Chichibabin (120). They are prepared by coupling under special conditions, diazotized 2-aminopyridine with 2-naphthol, resorcinol, cresol, or other phenols.

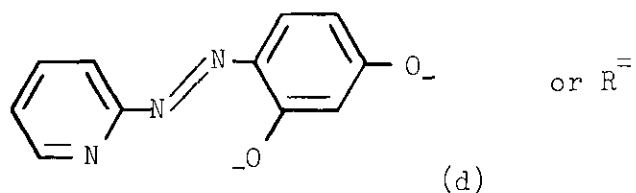
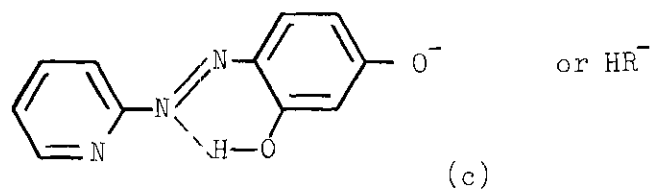
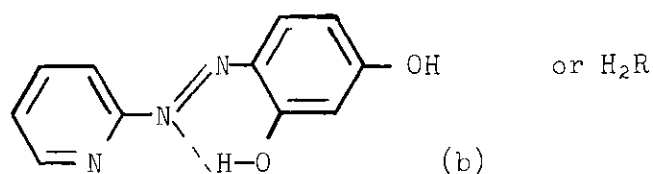
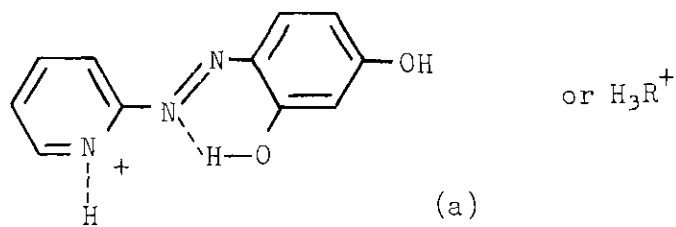
Of the possible pyridine-azo compounds, one of the most frequently used is 4-(2-pyridylazo)resorcinol (PAR). A distinct advantage of this reagent is that PAR and its colored metal chelates are water soluble. The reagent is only slightly soluble in hot ethanol and slowly precipitates upon cooling the solution. PAR is readily soluble in acids or alkalies to give solutions ranging from yellow to orange in color. Aqueous solutions are stable for more than a year.

#### Properties of PAR in Aqueous Solutions

##### Effect of pH

Aqueous solutions of PAR vary in color from yellow to orange depending upon the pH of the solution. Hnilickova and Sommer (121) carried out a spectrophotometric study of the behavior of PAR over a wide range of acidity and established that six different species exist. Over the pH range 0-14, solutions of PAR exhibit four different colors.

At pH values less than 2 the pyridine nitrogen atom is protonated and the cation  $H_3R^+$  is formed. In the pH range 2.1 to 4.2 the undissociated form  $H_2R$  is the predominant species. In the pH region 4.2 to 7.0 the hydroxyl proton in para-position to the azo group, dissociates producing the anion  $HR^-$ . The hydroxyl proton in the ortho-position dissociates in the pH region 10.5-13.5 forming the anion  $R^{-2}$ . Thus, there exists one protonated form (a), one undissociated form (b), and two dissociated forms (c) and (d).



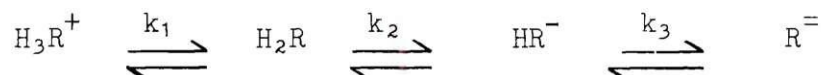
Hnilickova and Sommer also described two other species of PAR in aqueous solution. They reported the formation of the species  $\text{H}_5\text{R}^{+3}$  and  $\text{H}_4\text{R}^{+2}$  in 90 and 50 percent sulfuric acid, respectively. The absorbance peaks of the various species which they reported are presented in Table 2.

Table 2 presents the correlations of absorbance maxima to PAR species as determined by several investigators in aqueous solutions. Iwamoto (122) reported absorbance spectra for PAR over the pH range 0-14 while Pollard and coworkers (123) obtained absorbance data for PAR at 21 pH increments between 1.0 and 13.0.

Figures 2 and 3 show absorbance curves obtained in this laboratory under the same pH conditions as described by Hnilickova and Sommer (121). The final data in Table 2 shows the correlation between absorbance maxima and PAR species obtained in this laboratory.

#### Acid Dissociation Constants of PAR

A number of workers have determined values for the dissociation constants. Table 3 lists the reported values obtained by the various workers for the following dissociations:



#### Composition and Structure of PAR Complexes

PAR forms colored chelates with a large number of metal ions. Absorption curves involving PAR and related reagents have been studied and it is probable that PAR reacts through the nitrogen atom of the pyridine ring, the nitrogen of the azo group being farthest removed from the pyridine ring and through the hydroxyl in the ortho-position to the azo group (123). Iwamoto (122) and Shibata (124) propose that PAR be

Table 2. Correlation of Absorbance Maxima to PAR Species  
in Aqueous Solutions

$H_5R^{+3}$	$H_4R^{+2}$	$H_3R^{+}$	$H_2R$	$HR^{-}$	$R^{-2}$	Reference
433	390	395	385	413	490	Hnilickova (121)
---	---	400-470	390	410	490	Iwamoto (122)
---	---	395	383	415	485	Pollard (123)
435	435	400-470	390	415	490	Present work

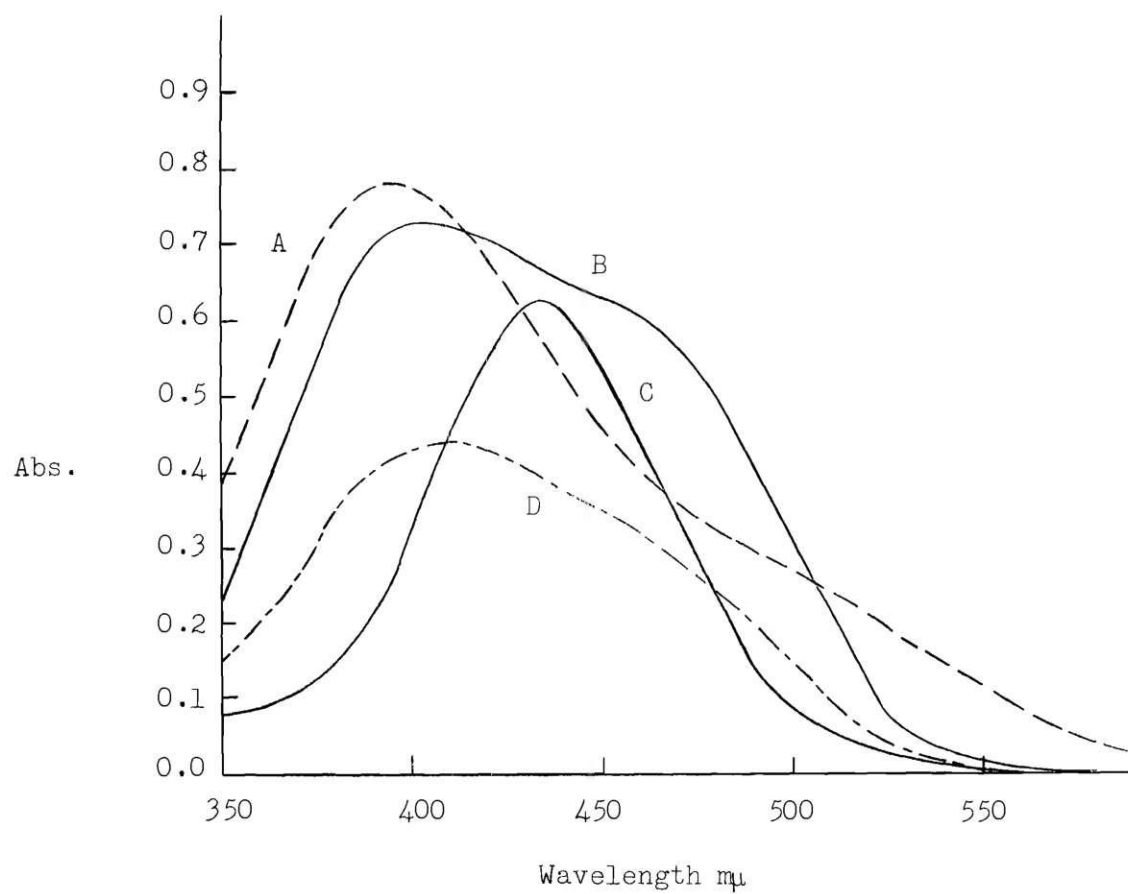


Figure 2. Spectral Curves of PAR Solutions

- A pH 4.5
- B pH 1.0
- C 16.2  $\underline{\text{F}}$   $\text{H}_2\text{SO}_4$  (90%)
- D 3  $\underline{\text{F}}$   $\text{H}_2\text{SO}_4$

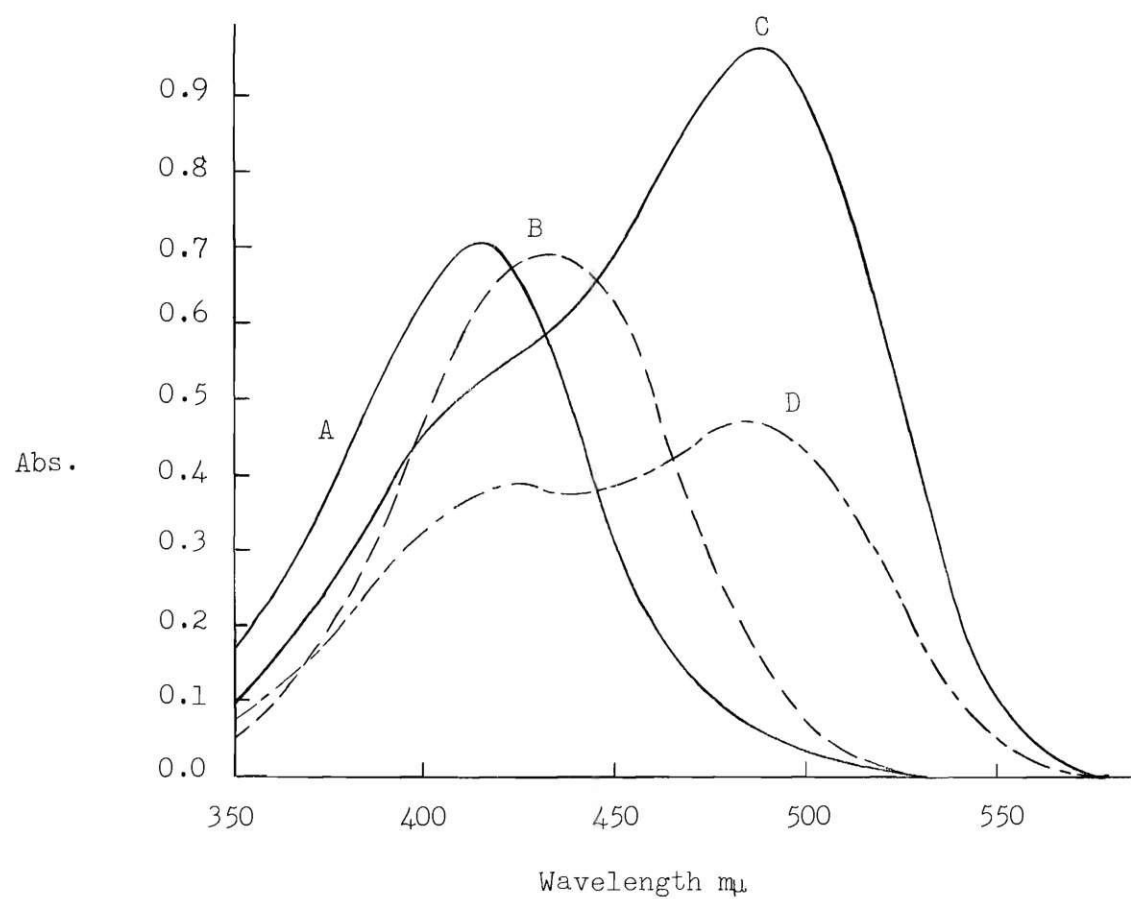


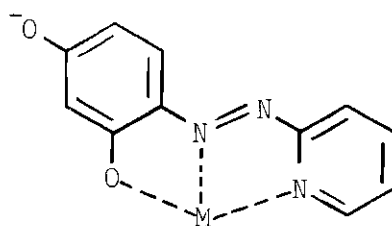
Figure 3. Spectral Curves of PAR Solutions

- A pH 7.0
- B 9.0 F H<sub>2</sub>SO<sub>4</sub> (50%)
- C pH 12.0
- D pH > 14

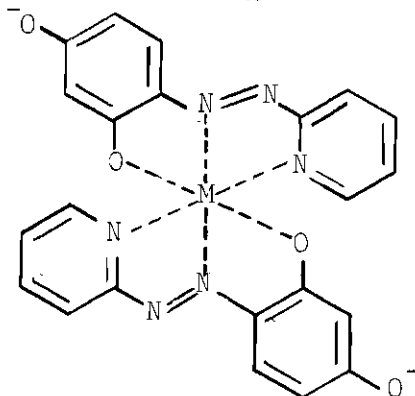
Table 3. Acid Dissociation Constants of PAR

Authors	$pK_1$	$pK_2$	$pK_3$
Iwamoto (122)	---	5.83	12.5
Hnilickova (121)	3.10	5.60	11.90
Frieser (125)	2.30	6.90	12.40
Pollard (123)	2.66	5.48	12.31
Dey (126)	2.57	6.20	11.50

considered to act as a terdentate ligand having the three donor atoms in a plane. Thus the 1:1 and the 1:2 complexes would have the structures A and B, respectively.



A



B

#### Application of PAR as a Photometric Reagent

Since its introduction as a metallochromic indicator by Wehber (127) in 1957, PAR has been investigated by many workers. The reagent reacts to form colored chelates with a large number of metals. In solutions 0.05 to 0.5 formal in sulfuric acid PAR reacts with copper, bismuth, zirconium, titanium, thallium, palladium, vanadium, niobium, and gallium. In solutions of pH about 2.5 to 6, PAR begins to react with lead, zinc, cadmium, cobalt, nickel, mercury, manganese, uranium, tantalum, lanthanum, indium, scandium, yttrium, aluminum, and thorium. In a



1 F ammonium hydroxide medium, PAR reacts also with calcium, barium, strontium, and silver.

PAR has been employed as a chromogenic reagent in the spectrophotometric determination of many elements. Table 4 lists the metals, the pH conditions for the formation of the complexes, and their characteristic properties.

Inspection of Table 4 may cause one to question the value of PAR as an analytical reagent since it has an extremely low selectivity. However, the overall evaluation must be based not on the reagent alone, but on the procedure as a whole. Here the judgment becomes much more favorable because of the application of masking reagents that in many cases allow a considerable increase in selectivity. Thus, for example, the procedure for the determination of niobium (142) is specific within the group of metals commonly accompanying this element. In many other cases a simple group separation considerably improves the situation. These facts in combination with the high sensitivity of the color reaction, the stability of the color developed, the stability of the reagent solution and the ease of operations make PAR, one of the outstanding chromogenic reagents.

Table 4. Photometric Methods Using PAR

Metal	Molar Ratio M:PAR	Absorbance Maximum $m\mu$	Molar Absorp- tivity	pH	Beer's Law ppm	Ref.
Bi	1:1	430	10700			121
Cd	1:2	495	57800	9		121
Co		510		7.0-9.0	0-1.4	128
Co	1:2	510	56000	3-10	.1-1	129
Co	1:2	510		6.8-8.2		130
Cu	1:1	522	12100	2.3-5.0		121
Cu	1:2	505	58900	5		121
Ga		510	28000	3.7-4.5	0.1-2.8	131
Ga	1:2	504	102000	7.0	0.04-0.6	132
Ga	1:1	493	21200	1.5-3.0		133
Ga	1:2	503	9900	3.5-5.0	0-0.1	133
Ga	1:1	500	32800	6.0-8.0	0.2-4.8	134
Ga		green filter		4.7-6.7	0.04-0.2	135
In		510	20000	3.5-4.5	0.2-4.6	131
In	1:2	510	86400	7.0		132
In	1:1	520	17100	4.0	0.2-8	133
In	1:1	500	32800	6.5-8.0	0.05-1	134
In	1:1	500	37700	2.7-8.0	0.02-1	136
In	1:1	510	32000			137
In	1:2	510	86400			138
Ni		494	73000	8.6-10.0	0.05-1	139
Nb	1:1	555	31200	5.8-6.5	0.4-4	140
Nb	1:1	550		5.8	0-0.7	141
Nb	1:1	550	38700	5.8	0.1-0.7	142
Nb	1:1	590	32300	5.0	0-0.8	143
Nb	1:1	540	23300	5.5		144
Nb	1:1	535		0.75 $\underline{F}$ HCl		145
Nb		550		5	0.05-1	146

Table 4. Continued

Metal	Molar Ratio M:PAR	Absorbance Maximum $m\mu$	Molar Absorp- tivity	pH	Beer's Law ppm	Ref.
Os	1:2	533		8.8	0.3-5	147
Pd	1:1	510	18400	4.0-7.0	0.2-2	109
Pd	1:1	440	18350	{0.05-3.5 F H <sub>2</sub> SO <sub>4</sub>	2-10	109
	1:1	630	9020		2-10	109
Pb	1:1	520	40000	10.0	0.2-4	148-149
Pb		520		10.0	0-5.0	128
Pb	1:1	512	10800	2.3-5.0		121
Pb	1:2	522	50200	5.0-8.0		121
Y	1:2	515	21000	5.5-7.0	0.5-4.0	121
La	1:2	515	17500	5.8-7.0	0.4-6.0	121
Ce	1:2	515	16000	6.0-7.0	0.4-7.0	121
Pr	1:2	515	15500	6.0-7.0	0.4-7.0	121
Nd	1:2	515	35000	6.0-7.0	0.5-6.0	121
Sm	1:2	515	42500	6.0-7.0	0.5-6.0	121
Eu	1:2	515	34000	6.0-7.0	0.5-6.0	121
Tb	1:2	515	29000	6.0-7.0	0.4-7.0	121
Dy	1:2	515	31000	6.0-7.0	0.4-7.0	121
Ho	1:2	515	28000	6.0-7.0	0.4-7.0	121
Er	1:2	515	50000	6.0-7.0	0.5-6.0	121
Tm	1:2	515	35000	6.0-7.0	0.5-6.0	121
Yb	1:2	515	26000	6.0-7.9	0.5-6.0	150
Sc	1:1	515	22000	6.2	0.05-2	151
Sc	1:1	530	14700	3.5-5.0	0.05-2.4	152
Ta	1:1	515	20400	6.0-8.0	0.04-4	140
Ta	1:1	535	16700	4.0-5.5	0.1-1.6	153
Th	1:4	500	38900	6.4-6.7	0.4-8.0	154
Th	1:2	510		3.0-6.0		131
Tl	1:1	520	18050	4.0-5.0	1-10	155
U		530		8.0	0-6.0	128

Table 4. Continued

Metal	Molar Ratio M:PAR	Absorbance Maximum $m\mu$	Molar Absorp- tivity	pH	Beer's Law ppm	Ref.
U		540		7.8	0.07-16	156
U	1:1	530	38700	8.0	0-7	157
V	1:1	550	36000	5.0-7.0	0.04-1	158
V	1:1	545		5.5-6.0		159
Zn	1:2	495	63400	5.3-7.5		121

## CHAPTER V

## EQUIPMENT AND CHEMICALS

Laboratory EquipmentSpectrophotometers

All of the absorbance curves were obtained with a Bausch and Lomb Spectronic 505 recording spectrophotometer. The analytical absorbance measurements were made with a Bausch and Lomb Spectronic 20.

Photometric Titrator

The photometric titrator used in the standardization of palladium stock solutions was that designed and built by Flaschka and Sawyer (160).

pH Meter

All pH measurements were made with a Leeds and Northrop No. 7664 pH meter. The device was calibrated with potassium acid tartrate (saturated solution, 25°C, pH 3.57).

Glassware

The usual laboratory glassware such as beakers and flasks were used as needed. All volumetric Class A glassware was used without additional calibration.

ChemicalsWater

Deionized water was used exclusively.

PAR

Indicator grade PAR from Dojindo and Company, Ltd., Kumamoto-shi,

Japan, was used.

A stock solution approximately  $10^{-3}$  F in PAR was prepared by dissolving 0.215 g of PAR in one liter of deionized water.

To obtain the working solution, 25 ml of the stock solution was diluted to 100 ml with deionized water. This solution was used only in the procedure at pH 7.0.

#### Disodium (Ethylenedinitrilo)tetraacetic Acid Dihydrate (EDTA)

Reagent Grade disodium EDTA was used for the preparation of all EDTA solutions used in this investigation.

#### Palladium

Reagent Grade palladium(II) chloride was used.

Standard Palladium Solution I (for Procedure I Chapter 6). A solution was prepared by dissolving 0.0888 g of palladium chloride in 500 ml of deionized water. Five milliliters of concentrated nitric acid was added and the solution diluted to one liter. The solution was then standardized by a titration with EDTA (62) to a photometric endpoint.

Standard Palladium Solution II (for Procedures I-V Chapter 7). A solution was prepared by dissolving 0.0888 g of palladium chloride in a minimum amount of water in a porcelain dish. About 10 ml of concentrated sulfuric acid and 1 ml of nitric acid were added and the solution heated to fumes. After cooling, the solution was transferred to a 1-liter volumetric flask and diluted to mark with distilled water. The solution was standardized by titration with EDTA (62) to a photometric endpoint.

#### Acids

Reagent Grade concentrated nitric, hydrochloric, sulfuric and phosphoric acids were used as required.

### Bases

Reagent Grade aqueous ammonia and sodium hydroxide pellets were used.

### Stripping Solution A

The solution was prepared by dissolving 6 g of sodium chloride, 5 ml of 85 percent phosphoric acid, and 170 ml of concentrated sulfuric acid in 500 ml of deionized water. After cooling, the solution was transferred to a 1-liter volumetric flask and diluted to mark with deionized water.

### Stripping Solution B

The solution was prepared by dissolving 14.8 g of mercuric sulfate and 170 ml of concentrated sulfuric acid in 500 ml of deionized water. After cooling, the solution was transferred to a 1-liter volumetric flask and diluted to mark with deionized water.

### Dimethylglyoxime Solution

Six grams of dimethylglyoxime was dissolved in 500 ml of 95 percent ethanol.

### Ethyl Acetate

Redistilled technical grade ethyl acetate saturated with 3 F sulfuric acid was used for all extractions. Saturation was accomplished by shaking 100 ml of ethyl acetate with 100 ml of 3 F sulfuric acid for 15 seconds, separating the phases and then shaking the organic layer again with another 100-ml portion of sulfuric acid.

### Sodium Chloride Solution

Fifty-eight grams of sodium chloride was dissolved in 500 ml of deionized water and diluted to 1 liter.

### Masking Solution

The masking solution was prepared in the following manner. Deionized water was saturated with sodium citrate, potassium chloride and EDTA and the pH adjusted to 7.0 by the addition of either solid citric acid or concentrated hydrochloric acid.

### Other Metal Salt Solutions

Reagent Grade metal nitrates or sulfates were used to prepare the desired solutions. Where these salts were not available, Reagent Grade metal was dissolved in sulfuric or nitric acid. If the metal was insoluble in these acids, it was dissolved in an appropriate manner and converted to the sulfate by fuming with sulfuric acid.

### Standardization of Palladium Solutions

An EDTA titration employing a photometric endpoint was used (62). An aliquot of the palladium solution was pipetted into a phototitrator cell and diluted with water. A solution containing about 0.2 g of potassium tetracyanonickelate (II) was then added to the slightly acidic palladium solution followed immediately by 5 ml of concentrated ammonium hydroxide. Murexide indicator was added next and the liberated nickel was titrated photometrically with EDTA at 440 m $\mu$ .



## CHAPTER VI

### THE DETERMINATION OF PALLADIUM AT pH 7.0

#### Introduction

During an investigation of the possibility of directly titrating palladium with EDTA to a visual endpoint, several metallochromic indicators were tested, including PAR. It was found that at about pH 7, PAR forms an intensely red-colored complex with palladium; but the color could not be discharged by the addition of EDTA even when added in considerable excess. The red complex also formed when PAR was added to a solution containing palladium already complexed by EDTA. Thus PAR could not be employed as the indicator in an EDTA titration. However, these results suggested the use of PAR as the chromogenic agent in a photometric determination of palladium, with EDTA present as a masking agent since the latter prevents the formation of the PAR complexes of most of the other metals.

#### Experimental

All photometric measurements were made using the equipment described in Chapter V. All of the reagents required for the experiments described in this section were prepared and standardized according to the procedures given in Chapter V.

#### Preliminary Investigation

In preliminary investigations absorbance curves of the palladium-

PAR complex and of PAR alone in the presence of EDTA were recorded, and the pH dependence of the absorbance was studied. Thereby it was found that a wavelength of 516 m $\mu$  and a pH of about 7 were suitable conditions for the determination. Next, experiments were conducted to study interferences. When PAR was added first and then EDTA to solutions containing palladium and an interfering metal, difficulties arose in the presence of some metals due to either incomplete or slow decomposition of their PAR complexes. It was, therefore, decided to proceed in the reverse order, that is, to add the EDTA first, next to adjust the pH and then to add the PAR. This order of addition has the further advantage that precipitation of some metals due to hydrolysis is avoided. Even with this modification, masking of some elements by EDTA was insufficient and additional masking reagents were investigated. Citric acid was found to be most effective. This reagent has the additional advantage of providing the buffer action required.

For masking some metals, citric acid alone was found to be quite adequate, while for others EDTA alone was satisfactory. In order to provide overall masking for a general procedure, it was decided that both reagents would be added in all cases. To do so is advantageous also from another point of view. It was observed that the transfer of palladium from its citrate complex to PAR proceeds extremely slowly, but is greatly enhanced in the presence of EDTA (see Table 5). This action may be explained in the following manner. The transfer of palladium from its citrate complex to EDTA is fast, as is the transfer from the EDTA complex to PAR. Thus in the presence of EDTA, the transfer of palladium from the citrate complex to PAR is speeded up. Another possible

explanation is to assume the formation of a fast reacting mixed complex containing palladium, EDTA, and citrate. The exact mechanism is not known, however, the effect is not concentration dependent and even a trace of EDTA is sufficient to promote the reaction. Table 5 also shows that the amount of EDTA present does not affect the absorbance of the palladium-PAR complex.

It was now necessary to record the absorbance curves of PAR and its palladium complex under the new solution conditions. These curves are presented in Figure 4. The absorbance maximum of the palladium-PAR complex still occurs at 516 m $\mu$ . For the highest sensitivity in a photometric determination, this wavelength should be chosen; however, at this wavelength the absorbance due to an excess of PAR cannot be neglected. To eliminate this effect, it is necessary either to measure the absorbance of the palladium-PAR complex at a longer wavelength with a loss of sensitivity, or to operate with a fixed amount of PAR both when obtaining the calibration curve and when making the actual determination. Since PAR stock solutions show excellent stability on storage, the latter alternative is best suited.

A close comparison of absorbance curves obtained in the presence of citrate (Figure 4) with those recorded in its absence reveals that citrate has a slight, enhancing effect on the absorptivity of the palladium-PAR complex. The enhancement as a function of the citrate concentration was studied as follows. When 0, 5, 15, and 30 ml of saturated sodium citrate solution were added to solutions containing fixed amounts of palladium, PAR, and EDTA, which were adjusted to pH 7.0 and then diluted to final volume, the eventual absorbance values obtained were 0.386,

Table 5. Effect of Sodium Citrate and EDTA on the Absorbance of the Palladium-PAR complex

EDTA *	Sodium Citrate *	Palladium $5 \times 10^{-4}$ F	Standard PAR sol.	pH	Absorbance after		
					5 Min	10 Min	15 Min
0	10	1	10	7.0	.066	----	.092
0	0	1	10	7.0	.130	.130	.130
10	0	1	10	6.7	.297	.300	.300
20	0	1	10	6.8	.301	.301	.301
30	0	1	10	6.8	.301	.301	.301
10	20	1	10	7.0	.314	.314	.315
20	10	1	10	7.0	.310	.313	.314
10	10	1	10	6.0	----	----	.317
10	10	1	10	8.0	----	----	.313

\* Saturated solutions.

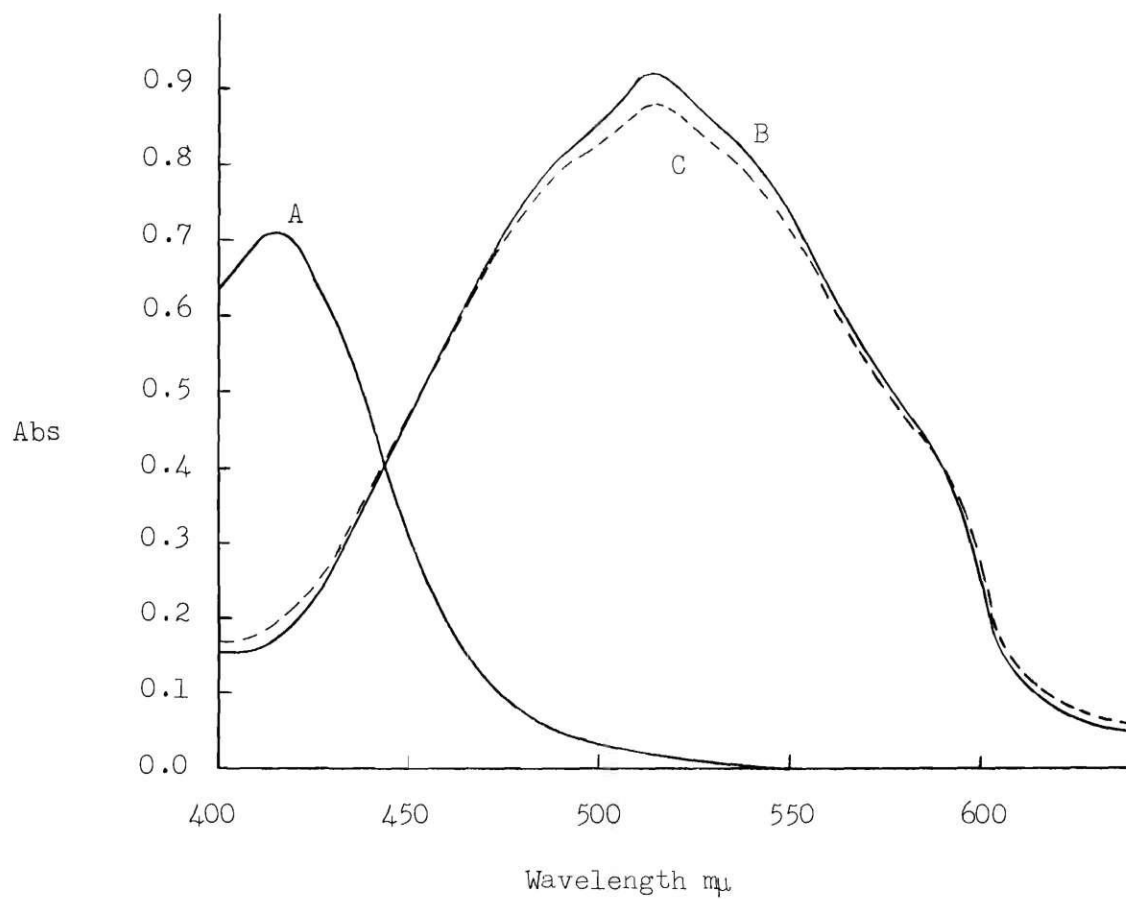


Figure 4. Absorbance Curves of PAR and Its Palladium Complex

- A PAR at pH 7.0
- B Palladium-PAR Complex in Presence of EDTA and Sodium Citrate
- C Palladium-PAR Complex in Presnce of EDTA

0.408, 0.407, and 0.408, respectively. From these data it was reasoned that any difficulties due to this effect are excluded if the citrate concentration is adjusted to a level where it no longer has any influence on the absorptivity. While addition of 5 ml of saturated citrate is sufficient, it was decided to employ 15 ml and thus establish a safe margin. For simplicity this solution was also saturated with EDTA, the amount of which has no effect on the absorbance of the palladium-PAR complex.

It was desirable to reexamine the pH dependence of the absorbance of PAR at 516  $m\mu$  and its palladium complex under the new solution conditions. The results of these investigations are presented in Figure 5. A plateau is observed between pH 6 and 8, and 6.5 and 9, for the palladium-PAR complex and for free PAR, respectively. Because of the well-developed and expanded plateaus, it is not necessary to exercise extreme care in controlling the pH.

It may be of interest to mention that during the initial studies of the pH effects, ammonium acetate was added to the solutions in order to provide some buffer action. When moderate amounts of this reagent were added to a solution already containing the palladium-PAR complex, no influence on the absorbance was observed. If, however, the ammonium acetate was added to the palladium solution before the addition of PAR, low absorbance readings resulted. This situation was not further investigated, but rather the decision was made to operate in the absence of ammonium ion.

A calibration curve was prepared by operating with solutions of pH 7.0 containing 15 ml of a solution saturated with EDTA and sodium citrate, and known amounts of palladium in a final volume of 50 ml. A

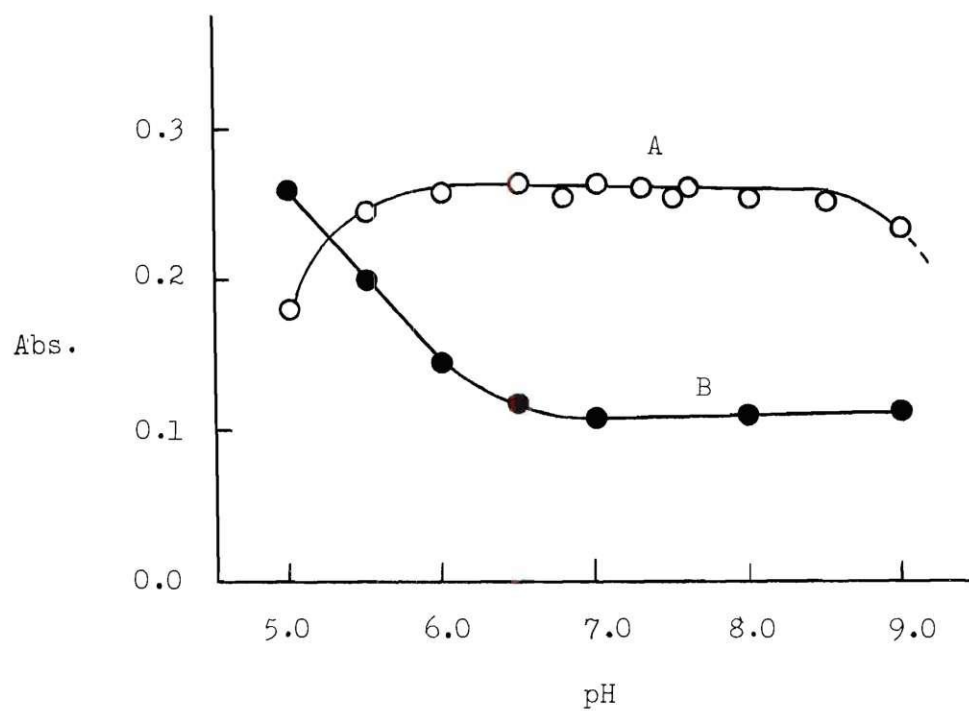


Figure 5. Dependence of Absorbance on pH

A Palladium-PAR complex

B Free PAR

straight line was obtained for concentrations of palladium up to 125  $\mu\text{g}$  Pd per 50 ml solution when measured at 516  $\text{m}\mu$ . For pure palladium solutions, the results were excellent.

The next step in the study was to investigate interferences. In some cases low results for palladium were obtained although the particular metals added were not expected to cause interference. An investigation of the situation revealed that chloride ion introduced with the metal solutions was responsible. An interference by chloride was not surprising since palladium is known to form stable chloro-complexes. The effect of chloride on the absorbance of the palladium-PAR complex is demonstrated by Figure 6. All solutions used in obtaining the data for the curves in this figure were diluted to a final volume of 50 ml. Line A (circles) was obtained from chloride-free solutions. Line B was obtained from solutions containing 10 ml of saturated potassium chloride. The slope of this line is significantly lower than that for line A. An additional series of measurements was made on solutions containing 10 ml of saturated potassium nitrate. The absorbance values (squares) are located exactly on line A thus indicating that the lower absorbance values in line B are not due to the considerable changes in ionic strength but are caused by the effect of the chloride ion.

It was now necessary to investigate the extent of competition between chloride and PAR for coordination with palladium. For this purpose, solutions were prepared which contained increasing amounts of chloride while holding the concentration of the other reactants (palladium, PAR, EDTA and citrate) constant. The results obtained are shown in Figure 7. These data show that no further influence is encountered above a certain



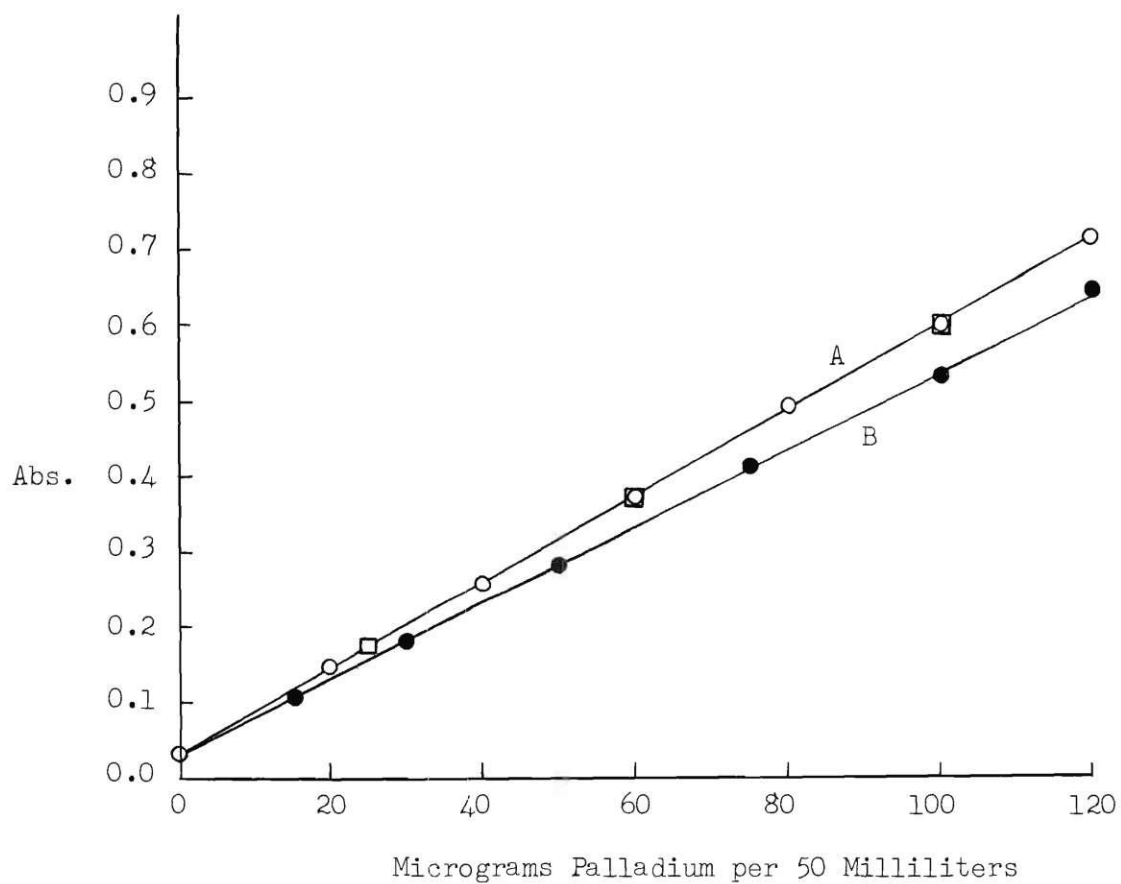


Figure 6. Palladium Calibration Curves.

A (Circles) No Salt Added

A (Squares) 10 ml Saturated Potassium Nitrate Added per 50 ml of Final Solution

B 10 ml Saturated Potassium Chloride Added per 50 ml of Final Solution

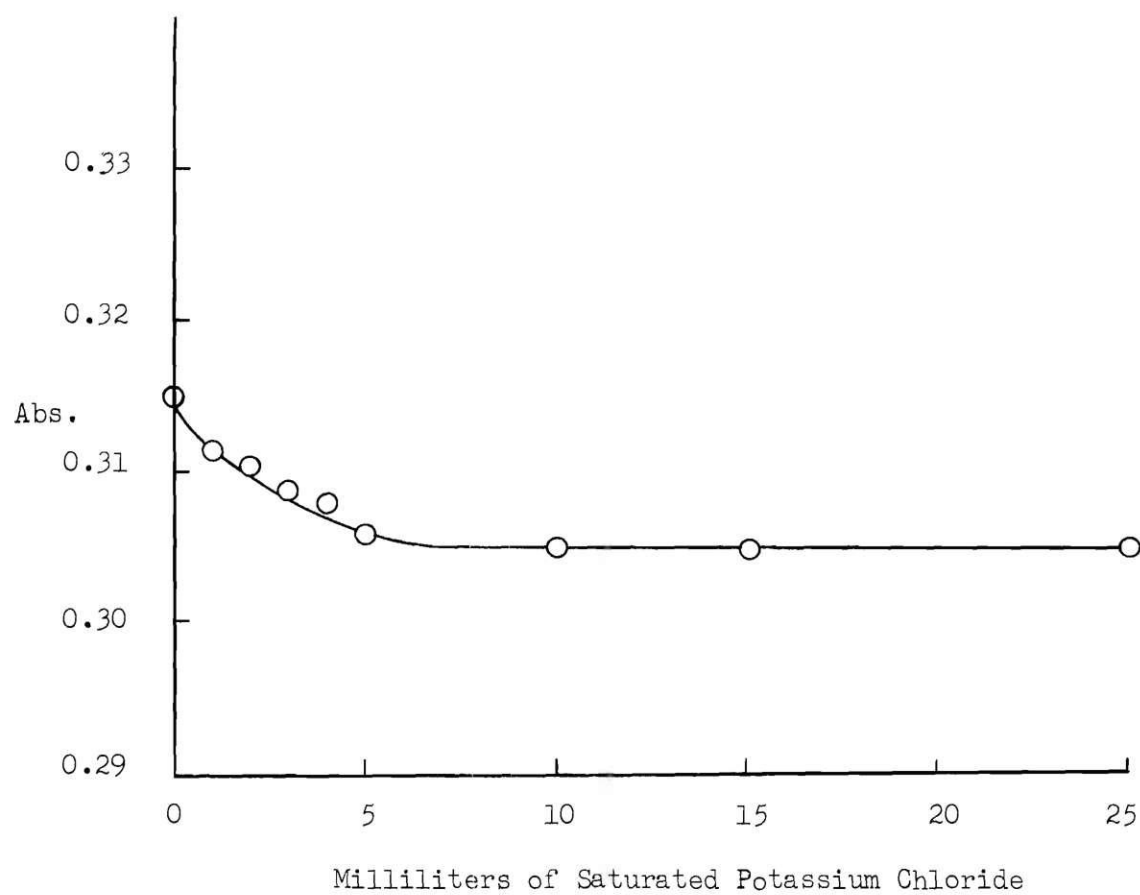


Figure 7. Influence of Chloride on the Absorbance of the Palladium-PAR Complex.

chloride concentration. The conclusion from this behavior is that chloride does not compete with PAR, but rather both chloride and PAR are coordinated by palladium with the formation of a mixed complex which has a slightly lower absorptivity than that of the pure palladium-PAR complex. Apparently, once the chloride concentration has reached a certain level, the equilibrium has its maximum shift towards the formation of the mixed complex and further increases in the chloride concentration have no longer any effect on the absorbance. More evidence for the existence of such a mixed complex will be presented in a later section. To prevent an interference by chloride, it is only necessary to establish its concentration at a level greater than that required for complete formation of the mixed complex. If accurate and reproducible results are to be obtained, it is apparent that a certain minimum concentration of chloride is necessary. The data from Figure 7 indicate that 15 ml of saturated potassium chloride per 50 ml of final solution is sufficient for this purpose. In order to simplify procedural details, it was decided to include the chloride in the masking solution; thus, this solution was saturated in citrate, EDTA, and potassium chloride.

While investigating the influence of chloride, a kinetic effect was encountered. Rate studies on the formation of the palladium-PAR complex were made and the results are presented in Figure 8. The data shows that as the concentration of chloride increases, the rate of formation of the palladium-PAR complex decreases. To insure complete color development, it is necessary to allow each solution to stand for a definite period of time after all reactants have been added. Based on these studies a 30-minute development time was chosen.

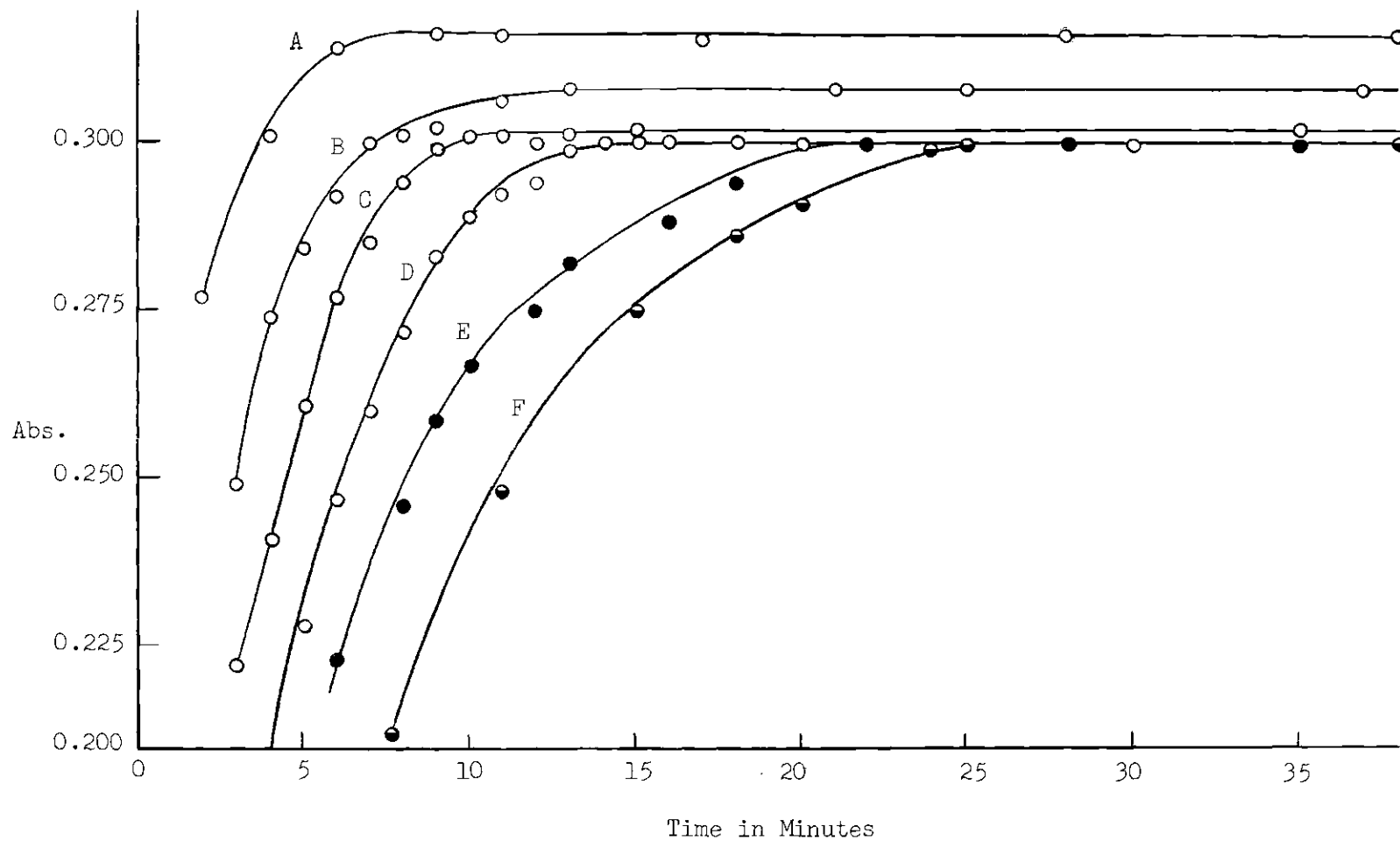


Figure 8. Influences of Chloride Concentration on Absorbance and Rate of Formation of the Palladium-PAR Complex. Milliliters of Saturated Potassium Chloride added per 50 ml of Final Volume. A, 0.0; B, 3.0; C, 5.0; D, 10.0; E, 15.0; F, 25.0

Since many metal ions form colored complexes with the masking reagents a special technique is employed to avoid any possible interference during the optical measurements. One aliquot of the sample solution is treated in the manner described and an identical aliquot is treated in exactly the same way except that the addition of PAR is omitted. The latter solution is used as the reference to set 100 percent transmission. Thus, any colored complexes formed in the sample solution with the masking reagents are also formed in the reference solution at exactly equal concentrations, and the interference is eliminated. For example, iron (III) with the masking agents forms a red-colored complex that absorbs strongly in the same region as the palladium-PAR complex, and, therefore, would interfere. However, by applying the technique described no difficulties occur and palladium can be determined in the presence of 600 times the molar amount of iron(III).

In an attempt to reduce the time required for the complete formation of the palladium-PAR complex, the effect of heating was investigated. Samples were prepared in the previously described manner and heated. It was found that in such palladium solutions in the absence of PAR a partial reduction to metallic palladium occurs. When the masking solution at pH 7.0 containing PAR was heated, it was found that a decomposition of PAR occurs and an orange precipitate forms which is insoluble in acids or bases. Whenever the solution was heated, low results for palladium were obtained. Since these problems occurred and since little time could be saved, no further attempts to influence the rate of complex formation were made.

### Procedure

Pipette an aliquot of the sample solution not exceeding 15 ml and containing up to 10  $\mu\text{g}$  of palladium per ml into a 50-ml beaker, add 15 ml of the masking solution and if necessary, adjust the solution to pH 7. (See Note 1.) Transfer the solution to a 50-ml volumetric flask, add 10 ml of the PAR reagent solution, dilute to mark with deionized water and allow to stand for 30 minutes. Treat an identical aliquot in the same manner as above, but omit the addition of the PAR. Use this aliquot to set 100 percent transmittance at 516  $\text{m}\mu$ . Measure the absorbance of the unknown sample solution. (See Note 2.) A calibration curve should be prepared by placing exactly known amounts of palladium standard solution I into 50-ml volumetric flasks and treating as described above. The absorbance should be measured at 516  $\text{m}\mu$  using deionized water as the reference.

### Notes

- (1) If a precipitate forms at this stage (as with tin(IV) and thallium(I)), stir until it is completely dissolved.
- (2) If the sample solution is colorless or if colorants present are known not to absorb at 516  $\text{m}\mu$ , distilled water may be used to set 100 percent transmittance.

### Results and Discussion

Figure 9 is a calibration curve prepared following the above procedure for the determination of palladium at pH 7.0. It shows a linear relationship between the absorbance and concentration from 0 to 3.26  $\mu\text{g}$  palladium per milliliter. The molar absorptivity calculated from these

data is  $2.88 \times 10^4$  liter/mole-cm. The sensitivity as expressed by Sandell (161) is  $0.0038 \mu\text{g}/\text{cm}^2$ . Sandell defines sensitivity as the number of micrograms of element, converted to the colored product, which in a column of solution having a cross section of  $1 \text{ cm}^2$  shows an absorbance of 0.001. The non-zero intercept is caused by the absorption of PAR at  $516 \text{ m}\mu$ .

Table 6 presents the results obtained for the determination of palladium at pH 7.0, when present alone and in the presence of other metal ions. The first entries in Table 6 show a quite satisfactory accuracy and precision of the method with palladium alone. On evaluating the data, one should consider that under the experimental conditions a variation of  $\pm 0.008$  absorbance units corresponds to approximately  $\pm 1 \mu\text{g}$  of palladium. The latter entries in the table indicate the tolerance levels of the other metals investigated during the interference studies.

Iron(III) can be tolerated in a ratio of 600:1. The iron-palladium ratio is limited more because of instrumental than chemical causes. The reference solution absorbs so strongly that with higher ratios of iron, it is impossible to set 100 percent transmittance.

An interesting effect is observed when both copper and nickel are present in a solution. Nickel alone can be tolerated in ratios as high as 1800:1 and copper alone up to about 800:1 without causing serious interference. This indicates that the effect of the interference due to copper is about twice that caused by nickel. When copper and nickel are present together in a solution, their combined molar ratio of metal to palladium cannot exceed 2000:1. Thus, it is necessary when estimating the combined molar ratio of copper and nickel, to multiply the copper concentration by a factor of two. For example, if nickel is present in a ratio

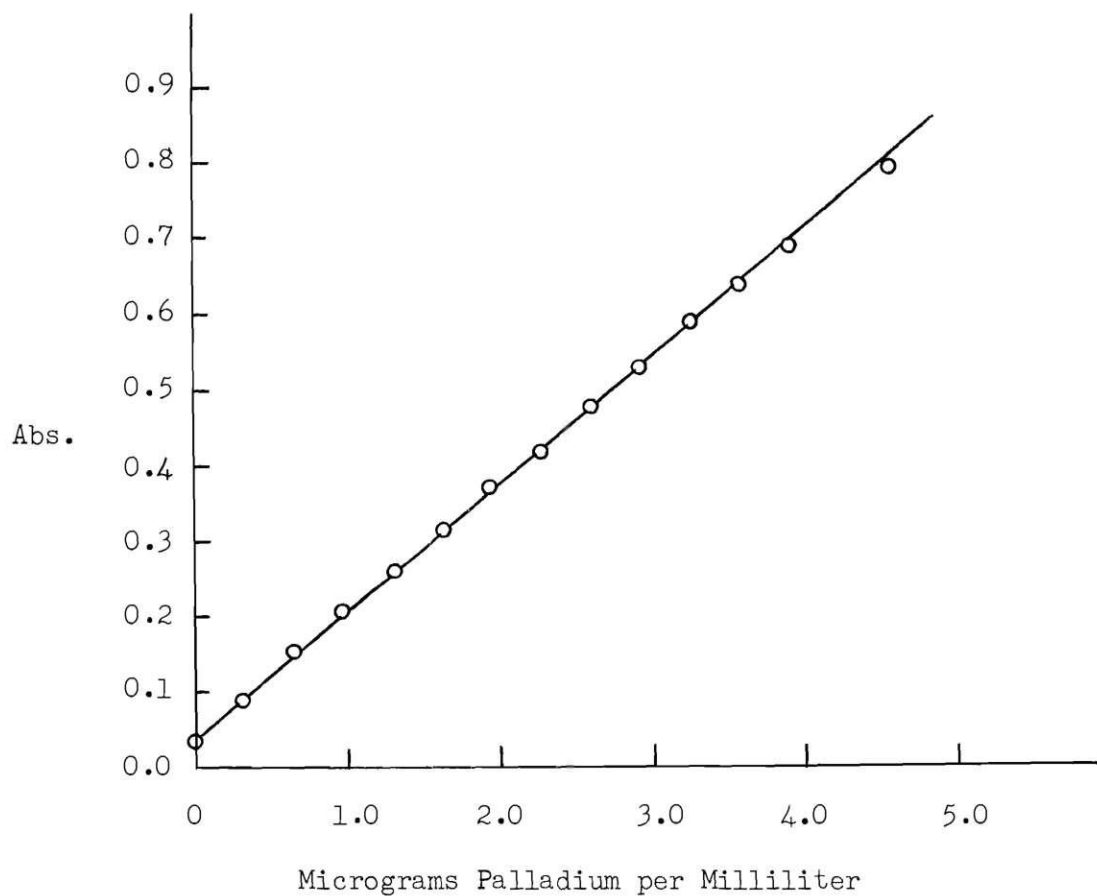


Figure 9. Calibration Curve for Palladium Determination at pH 7.0



Table 6. Results of Palladium Determinations at pH 7.0

Added	<u>μg Palladium</u>		Metal Ion M added	Mole Ratio M:Pd
	Found	Diff.		
36.5	37.1	+0.6	-----	-----
60.9	60.3	-0.6	-----	-----
	60.3	-0.6	-----	-----
	60.9	0.0	-----	-----
	60.9	0.0	-----	-----
	62.7	+1.8	-----	-----
	60.9	0.0	-----	-----
	60.9	0.0	-----	-----
	61.5	+0.6	-----	-----
	62.7	+1.8	-----	-----
	60.9	0.0	-----	-----
73.1	73.7	+0.6	-----	-----
60.9	61.5	+0.6	Li <sup>+1</sup>	2000:1
60.9	60.9	0.0	Be <sup>+2</sup>	2000:1
60.9	61.5	+0.6	Mg <sup>+2</sup>	2000:1
	61.5	+0.6	Ca <sup>+2</sup>	2000:1
	61.5	+0.6	Sr <sup>+2</sup>	2000:1
	61.5	+0.6	Ba <sup>+2</sup>	2000:1
	60.9	0.0	Sc <sup>+3</sup>	2000:1
	60.9	0.0	Y <sup>+3</sup>	2000:1
	60.9	0.0	La <sup>+3</sup>	2000:1
	60.9	0.0	Ce <sup>+3</sup>	2000:1
	60.9	0.0	Pr <sup>+3</sup>	2000:1
	60.9	0.0	Nd <sup>+3</sup>	2000:1
	60.9	0.0	V <sup>+4</sup>	2000:1
	63.3	+2.7	V <sup>+5</sup>	200:1
>152	----	----	Nb <sup>+5</sup>	200:1
90.7	+29.8		Ta <sup>+5</sup>	200:1

Table 6. Continued

Added	<u>μg Palladium</u>		Metal Ion	Mole Ratio
	Found	Diff.	M added	M: Pd
60.9	61.5	+0.6	Cr <sup>+3</sup>	2000:1
	61.5	+0.6	Cr <sup>+6</sup>	2000:1
	58.4	-2.5	W <sup>+6</sup>	2000:1
	60.9	0.0	Mn <sup>+2</sup>	2000:1
	61.5	+0.6	Fe <sup>+3</sup>	600:1
12.2	12.2	0.0	Os <sup>+3</sup>	1000:1
60.9	62.7	+1.8	Rh <sup>+3</sup>	200:1
12.2	12.2	0.0	Rh <sup>+3</sup>	2000:1
60.9	61.5	+0.6	Ni <sup>+2</sup>	1800:1
	61.5	+0.6	Cu <sup>+2</sup>	600:1
	62.1	+1.2	Cu <sup>+2</sup>	1000:1
	60.9	0.0	Zn <sup>+2</sup>	2000:1
	60.9	0.0	Cd <sup>+2</sup>	2000:1
	60.9	0.0	Hg <sup>+2</sup>	2000:1
	60.9	0.0	Al <sup>+3</sup>	2000:1
	60.9	0.0	Ga <sup>+3</sup>	2000:1
	60.9	0.0	In <sup>+3</sup>	2000:1
	60.3	-0.6	Tl <sup>+1</sup>	2000:1
	62.1	+1.2	Sn <sup>+4</sup>	1800:1
	61.5	+0.6	Pb <sup>+2</sup>	2000:1
	61.5	+0.6	As <sup>+3</sup>	2000:1
	60.3	-0.6	As <sup>+5</sup>	2000:1
	60.9	0.0	Bi <sup>+3</sup>	2000:1
	60.9	0.0	Se <sup>+4</sup>	2000:1
	62.7	+1.8	Th <sup>+4</sup>	2000:1
	62.1	+1.2	Th <sup>+4</sup>	2000:1
	60.9	0.0	IO <sub>2</sub> <sup>+2</sup>	2000:1

of 800:1 (metal to palladium) then copper can be tolerated up to 600:1.

Both tin(IV) and thallium(I) form precipitates upon the addition of the masking solution and stirring is required until complete dissolution is obtained (about one hour) before further processing the sample.

The following metals are not masked and interfere: niobium(V), tantalum(V), cobalt(II), and platinum(IV), all of which react with PAR and cause high results. The reaction of platinum(IV) with PAR is very slow and the absorbance continues to increase gradually as the solution is allowed to stand. Iridium(III), which by itself does not react with PAR, causes low results. No explanation for this amazing fact can be given. Iron(II), silver(I), and titanium(IV) precipitate upon addition of the masking solution and low results are obtained due to coprecipitation of palladium. The effect is especially pronounced with silver. Iron(II) was included in the study only because of theoretical interest, but this ion will hardly ever be encountered in an actual analysis. Of equally low practical importance is the interference caused by tin(II) when added to the palladium sample solution. This ion reduces PAR and probably on prolonged standing also palladium. Gold(III) is reduced to metallic gold in the presence of EDTA. The uranyl ion is not masked by the masking solution and forms a red-colored complex with PAR. This interference can be easily eliminated, however, by addition of sodium bicarbonate which masks the uranyl ion.

Since chloride affected the palladium-PAR complex, it was suspected that other anions capable of forming complexes with palladium would also have a detrimental effect on the procedure. Cyanide, thiosulfate, iodide, bromide, and thiocyanate were all found to fall into this category. In

some cases the complexes are so stable that no palladium-PAR complex is formed (e.g., cyanide) while with others only a reduction in the absorbance was observed (e.g., bromide). Because it is not difficult to avoid introduction of these ions into the solution when processing the sample, they do not present any serious practical difficulties and no further studies were conducted.

## CHAPTER VII

THE DETERMINATION OF PALLADIUM IN 3 F SULFURIC ACIDIntroduction

While conducting the investigation described in the preceding chapter, an article by Busev and Ivanov (109) came to our attention.\* These workers reported the application of PAR to the determination of palladium in a strongly acidic medium, utilizing an extraction of a green palladium-PAR complex which was formed. A study of this approach was of interest with respect to some of the elements that interfered at pH 7, especially platinum and cobalt. Busev and Ivanov studied the influence of many metal ions on the method; however, in no case did they give any indication of the amount of foreign metal that was tested. They stated that platinum does not interfere, but no mention was made about the influence of cobalt. It was therefore decided that an examination of this approach should be undertaken in an effort to prevent some of the interferences that occurred in the procedure when carried out at pH 7.0. During this investigation a number of problems were encountered that were not mentioned by Busev and Ivanov, and which required additional studies. These studies led to several interesting and valuable modifications of the general procedure that allow an increase in the overall sensitivity for the determination of palladium.

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\* All comments about the paper by Busev and Ivanov refer to the English translation as it appeared in the Journal of Analytical Chemistry of the U.S.S.R. Vol. 19 No. 2, 1964, p. 212.

## Experimental

All photometric measurements were made using the equipment described in Chapter V. All of the reagents required for the experiments described in this section were prepared and standardized according to the procedures given in Chapter V.

### Preliminary Investigation

#### Non-extraction Approach

The initial approach in our investigation of the reactions described by Busev was to develop the green palladium-PAR complex in a sulfuric acid medium and to measure the absorbance in the aqueous medium without applying an extraction. The absorbance curves of PAR and its palladium complex in 3 F sulfuric acid are presented in Figure 10. The curve of the palladium-PAR complex in aqueous medium (curve C) shows peaks at 416 and 580 m $\mu$ . For highest sensitivity, the peak at 416 m $\mu$  should be used. However, free PAR absorbs so strongly at this wavelength (curve B) that even operating with a fixed amount of PAR as described in Chapter VI is not possible. Therefore, one must accept lower sensitivity and measure the absorbance at 580 m $\mu$ , where the free reagent has no influence. Exclusion of an optical interference by foreign ions may be accomplished by applying the technique of using a PAR free aliquot of the sample as the reference as described in Chapter VI.

Effect of Chloride. Preliminary studies showed that excellent results could be obtained when analyzing solutions containing only palladium. The effects of platinum and cobalt were studied next, and, as reported by the Russian authors (109), platinum did not cause an interference. The

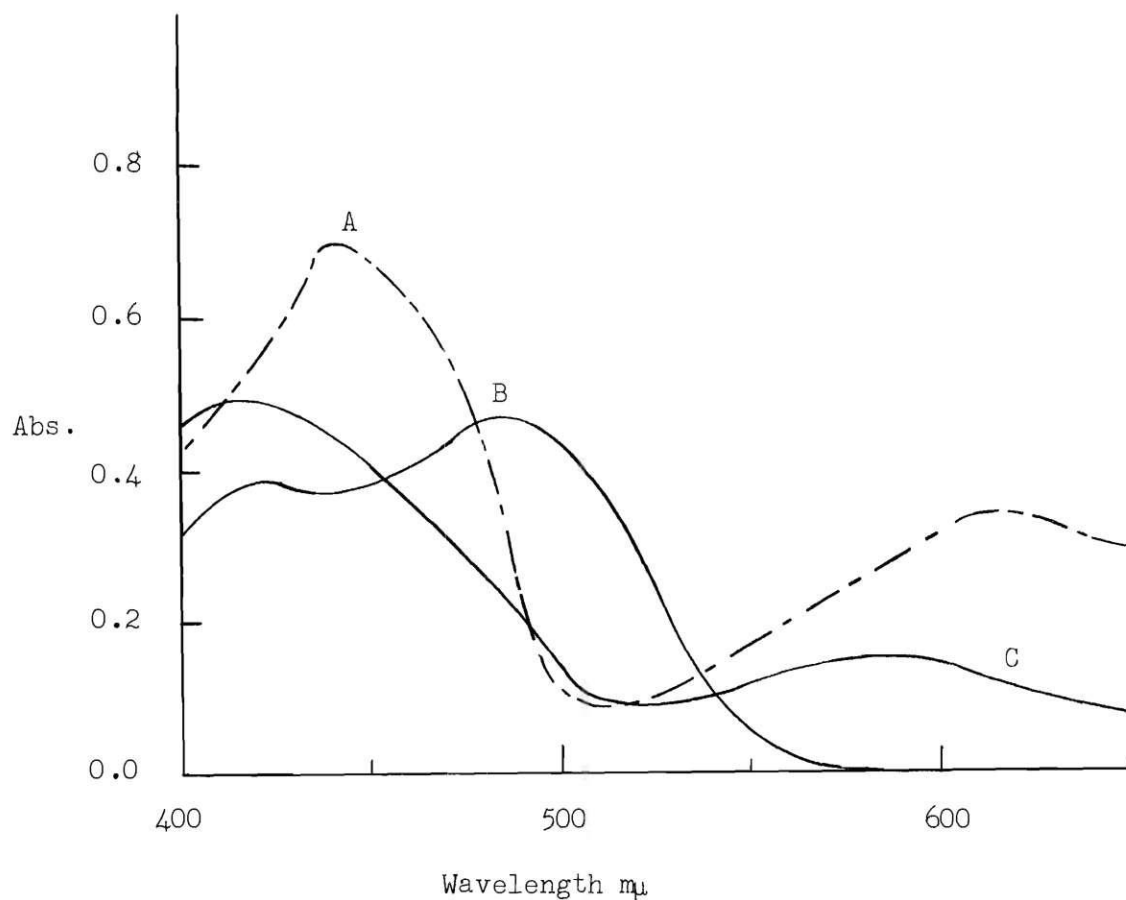


Figure 10. Absorbance Curves of PAR and Its Palladium Complex

- A Palladium-PAR Complex Extracted into Ethyl Acetate from 3 F Sulfuric Acid.
- B PAR in Aqueous 3 F Sulfuric Acid.
- C Palladium-PAR Complex in Aqueous 3 F Sulfuric Acid.

results in the presence of cobalt, however, were rather surprising. With increasing amounts of that metal, the recovery of palladium was found to decrease. The same phenomenon was encountered with several other metals, which for theoretical reasons should not interfere and were actually mentioned in Busev's paper as not interfering. Several attempts were made to solve this problem including a study of the systems using hydrochloric acid as the medium rather than sulfuric acid. It was found that in such solutions no green color developed at all. This clearly indicated that chloride ions were capable of blocking the reaction between PAR and palladium and offered a possible explanation of the difficulties previously encountered. Indeed, the metals that were used for the interference studies had been added as their chlorides and the palladium solutions that were used at this point of the investigation had been prepared in the same manner as described by Busev, namely, by dissolving palladium chloride in water, containing a small amount of hydrochloric acid to prevent hydrolysis. As will be seen from later studies on the effect of chloride, its amount present in the palladium solutions was not sufficient to fully prevent the formation of the green complex, but simply to cause a lower absorbance value to be obtained. When studying palladium alone in 3 F sulfuric acid, the ratio of chloride to palladium remained constant, the absorbance was proportionally low, the calibration curve was still straight and the effect went unobserved. When, however, additional chloride was introduced with the solutions of other metals during the interference studies, inconsistent results for palladium were obtained.

All further investigations were therefore performed with chloride free palladium solutions obtained by fuming a weighed amount of palladium



chloride with sulfuric and nitric acids and diluting with water to a definite volume. In addition, all metal solutions used in the interference studies were prepared from either the metal sulfates or nitrates. Under these conditions neither cobalt nor the other metals previously causing disturbance interfered. When operating in sulfuric acid medium, it is therefore mandatory that the formation of the palladium-PAR complex take place in the absence of chloride. Thus, for actual analyses the sample solution must either be prepared with exclusion of chloride, or if this is necessary for dissolving the sample, it must be removed before developing the green color. It is interesting to note that when a solution of platinum chloride is added no interference was observed. The chloro complexes of platinum obviously are sufficiently stable to keep the chloride bound to the platinum, thus preventing interference.

Even though precipitation of several metals occurs in 3 F sulfuric acid, no particular difficulties are encountered. Since no coprecipitation of palladium or its PAR complex occurs, filtration is a simple remedy. For the details of this approach, see Procedure I.

#### Extractive Approach

Application of an extraction to the palladium-PAR complex formed as described above was studied next because it offers two important advantages. First, the sensitivity of the method can be increased by extracting the complex from a large aqueous into a smaller, nonaqueous phase. Second, the palladium-PAR complex can be separated from many other absorbing species, thus eliminating the need for a special reference solution.

Effect of Chloride. An attempt was made to extract the green palladium-PAR complex into ethyl acetate as recommended by Busev and Ivanov;

however, the complex remained in the chloride free aqueous phase. This situation was rather unexpected but was clarified after a few further experiments. It was found that if a small amount of sodium chloride was added to either the aqueous or organic phase, the green complex was completely transferred into the ethyl acetate. This phenomenon may be explained in the following manner. The green palladium-PAR complex forms in a 1:1 molar ratio but a single positive charge remains, thus causing the complex to be hydrophilic. Upon addition of sodium chloride, additional coordination of chloride takes place, the charge is neutralized and the uncharged mixed complex formed is readily soluble in the organic phase.

Thus, a peculiar situation exists. On one hand, chloride, if initially present prevents the full development of the green color. On the other hand, a certain minimum amount of chloride is necessary in order to make the extraction of the green complex possible.

These facts offer some hint as to why the Russian authors did not mention anything about the influence of chloride. We suspect that Busev and Ivanov performed all of their investigations with either one palladium stock solution, or several solutions prepared in identical manner. If this is the case, then they would not have encountered difficulties provided large amounts of chloride were not added during their interference studies. Since no concentrations for the interfering elements are given in the Russian paper, we further suspect that the metals were either added as salts other than chlorides, or that the additions were sufficiently small, so that even in case chlorides were used, the chloride concentration never reached the level where noticeable effects resulted. The authors did not describe a procedure and were also scarce with information

in other respects so that more valid conclusions cannot be drawn.

An extensive investigation of the influence of chloride was undertaken next. At first the relationship between the concentration of chloride and the absorbance of the green complex was studied. For this purpose fixed amounts of palladium were placed in volumetric flasks and varying amounts of chloride added. Next enough sulfuric acid was introduced so that its concentration upon dilution to final volume was 3 formal, and finally a fixed amount of PAR was added. The solutions were diluted to mark and the absorbance measured at 580 m $\mu$  after a definite period of standing. For final chloride molarities of 0.00, 0.02, 0.04, 0.12, 0.16, 0.20, 0.40, 0.60, and 0.80, the percentage recoveries of palladium were respectively: 100, 94, 91, 77, 69, 63, 40, 25, and 21. From these data, it is clear that relatively small concentrations of chloride are sufficient to considerably impair the full development of the green color.

It was also observed that the absorbance reading changed with time. Therefore, rate studies were made which yielded quite interesting results as can be seen from Figure 11. Curve A shows the development of the green color as a function of time in the absence of chloride. Complete complexation is reached after about ten minutes. With increasing concentrations of chloride, a decrease in the rate of formation of the palladium-PAR complex is found. It is also interesting to note that in the presence of chloride, the absorbances never reach the value obtained in the absence of chloride, regardless of how much time is allowed. It is seen that after a certain period, the absorbance actually starts to decrease. These results seem to indicate that at least two reactions are taking place

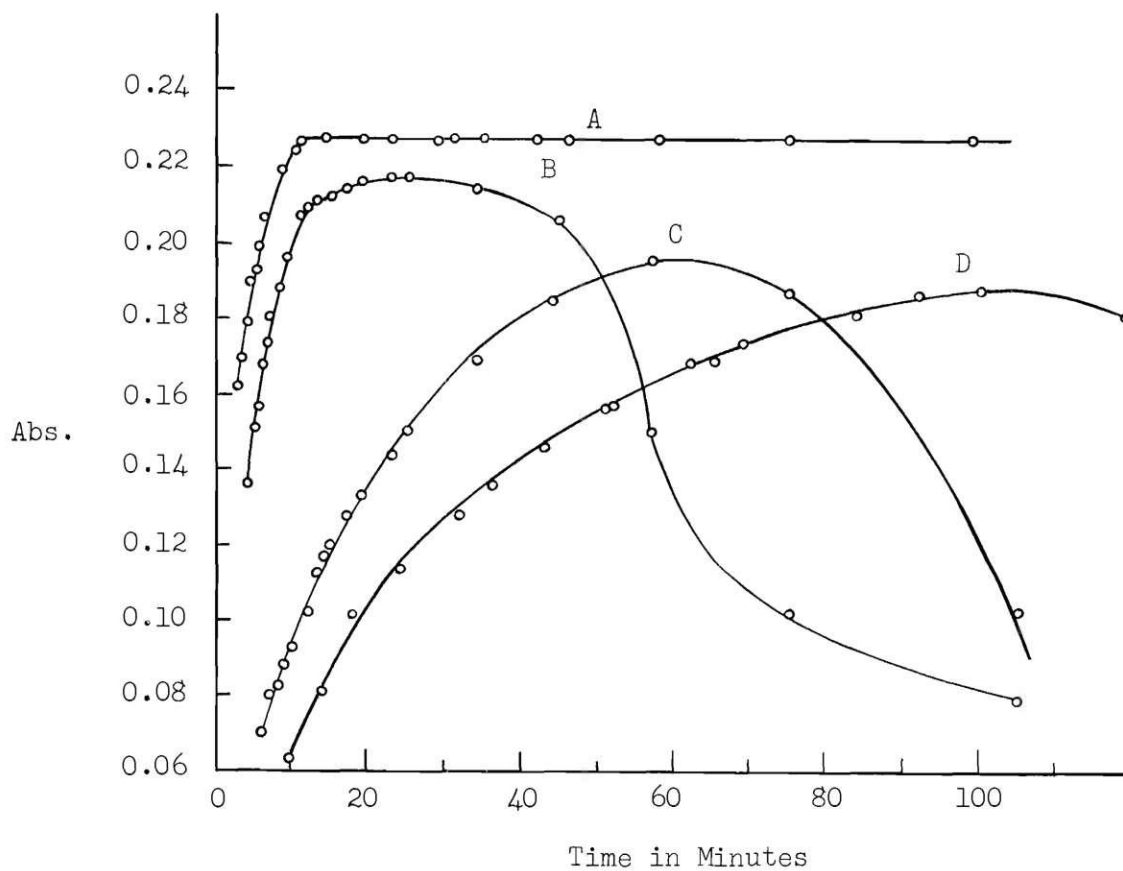


Figure 11. Influence of Chloride Concentration and Time on the Formation of the Palladium-PAR Complex in Aqueous 3 F Sulfuric Acid

- A No Chloride
- B 1000:1 Mole Ratio Chloride to Palladium
- C 6000:1 Mole Ratio Chloride to Palladium
- D 12000:1 Mole Ratio Chloride to Palladium

concurrently, but at different rates. First, PAR is successful either in removing some palladium from its chloro complex or in forcing the formation of a mixed complex. Second, it appears that a decomposition takes place, probably a reduction of the palladium as indicated by the formation of a brownish turbidity.

The influence of chloride in the extraction of the palladium-PAR complex with ethyl acetate was investigated next. In this study the green complex was allowed to form in the chloride-free solutions and then varying amounts of chloride were added and the extraction with ethyl acetate effected. Two ethyl acetate extractions were used, employing a 15-ml portion followed by a 10-ml portion. The extracts were combined and made up to exactly 25-ml with ethyl acetate. The absorbance curve of the green complex in ethyl acetate was slightly different from that in aqueous sulfuric acid (see Figure 10, curves A and C). The curve still has two absorbance maxima; however, they have been shifted to 440 and 616  $m\mu$ , respectively. The analytical absorbance measurements were made at 616  $m\mu$  to avoid interference from any free PAR extracted by the ethyl acetate. The absorbance values were plotted versus the chloride concentration and the corresponding graph is shown in Figure 12. As can be seen, there is an extended plateau between about 100:1 and 18000:1 mole ratio of chloride to palladium. Since such a wide plateau exists, an appropriate adjustment of the chloride concentration prior to extraction is not difficult. Whether the chloride is added to the aqueous phase or less conveniently to the ethyl acetate makes no difference for the extraction. Although a considerable amount of chloride is always present in the organic phase after equilibration is achieved, it has no

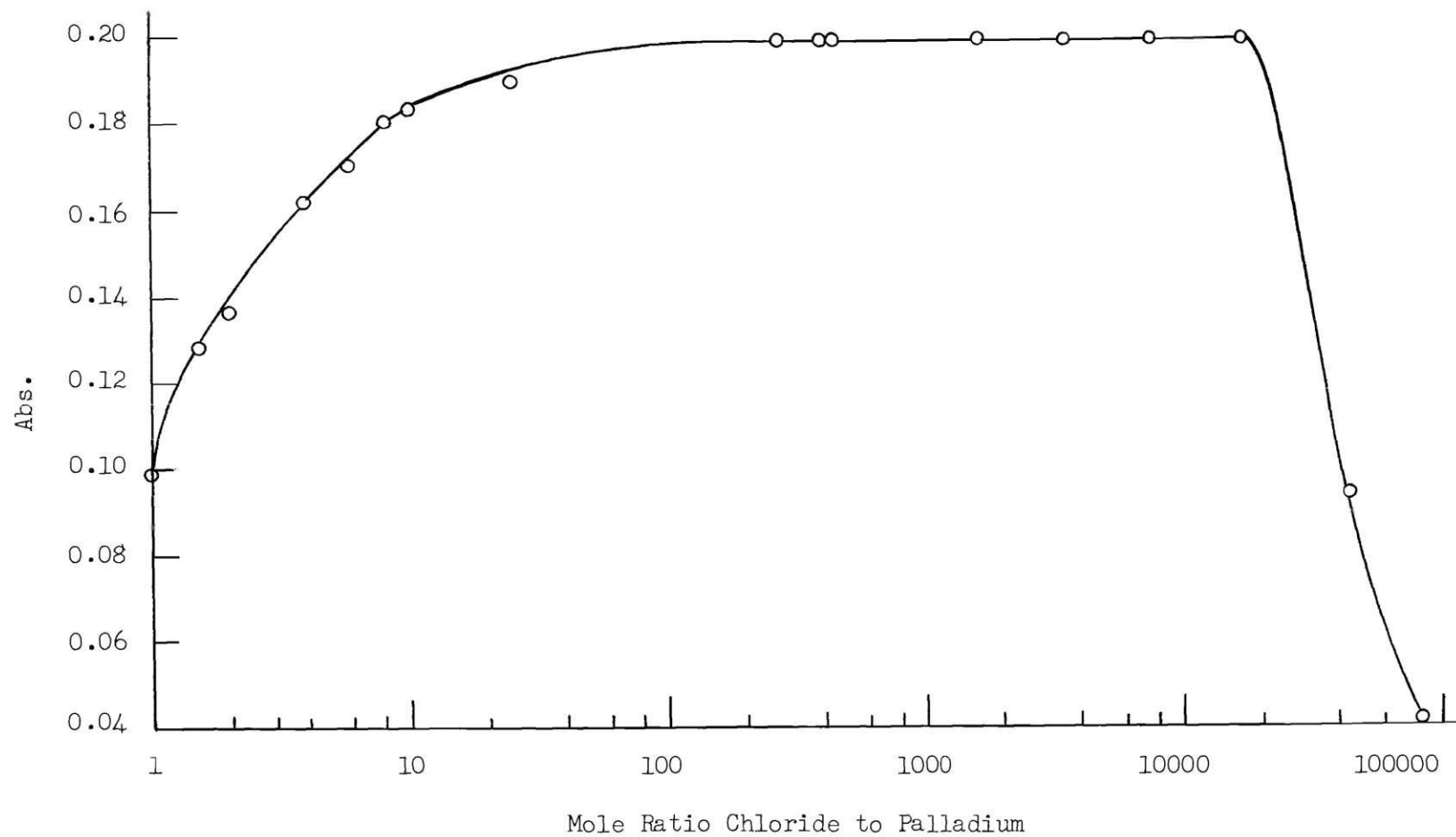


Figure 12. Influence of Chloride on the Extraction of the Palladium-PAR Complex from 3 F Sulfuric Acid into Ethyl Acetate

influence on the green complex and the color is stable over a prolonged period of time.

It is of interest to compare the action of chloride in sulfuric acid media with that in solutions of pH 7 as described in Chapter VI. In the latter medium the absorbance of the palladium-PAR complex decreases slightly until a certain concentration of chloride is reached; above that level no further influence is noticed. Apparently, chloride cannot successfully compete with the PAR and is only able to enter the palladium-PAR complex with formation of a mixed complex that has a slightly lower absorptivity. In acidic medium, however, chloride not only causes the formation of a mixed complex, but is capable of slowly removing palladium from the PAR complex. In addition the mixed complex existing in neutral solution is stable while that formed in acidic medium is subject to reductive destruction.

On the basis of the findings relevant to the determination of palladium in acid solutions, a procedure was developed which called for the formation of the green color in the absence of chloride, addition of a small amount of chloride, and immediate extraction with ethyl acetate. As recommended by the Russian authors, the ethyl acetate employed in the extraction was saturated with 3 F sulfuric acid just before use. In agreement with Busev's statement, the transfer of the green complex to the organic phase is essentially complete with one extraction. However, because some droplets cling to the walls and stem of the separatory funnel, a clear one-step phase separation is difficult and it was, therefore, decided to extract with two portions of ethyl acetate.

Busev states that no free PAR is extracted from solutions more

than 4.25  $\text{F}$  in sulfuric acid. This fact was confirmed; however, under this condition the distribution coefficient of the green complex is much less favorable and carrying out the extraction in 3  $\text{F}$  sulfuric acid is preferable because it requires the minimum number of extraction steps. In solutions about 3  $\text{F}$  in sulfuric acid the amount of free PAR passing into ethyl acetate varies from experiment to experiment, probably because of slight acidity changes. Thus it is not recommended to measure the absorbance at 540  $\text{m}\mu$  even if a fixed amount of PAR is added to the original solution. The absorbance of the palladium-PAR complex must be measured at 616  $\text{m}\mu$  where the sensitivity is lower, but no interference due to coextracted chromogenic reagent occurs.

#### Special Modifications

The solutions to several of the problems that were encountered during this investigation proved to be extremely useful in later modifications to the basic extractive approach for the determination of palladium. These modifications allowed an increase in the sensitivity of the basic procedure.

Removal of Free PAR. As previously pointed out, the measurement of the absorbance at 440  $\text{m}\mu$  where the absorptivity is approximately twice that at 616  $\text{m}\mu$  would be possible if no free PAR were extracted or if any extracted PAR could be removed. Such a removal is readily achieved by washing the combined extracts with aqueous 3  $\text{F}$  sulfuric acid containing a small amount of chloride. While the free PAR is stripped by the aqueous phase, the green complex remains in the organic phase. This technique has the potential advantage that some other colored species that are extracted into ethyl acetate may also be stripped from the organic



phase. Iron(III) is extracted as its chloro complex into ethyl acetate; however, it is not removed by the above stripping procedure. The yellow ferric-chloro complex does not interfere when the absorbance is measured at 616  $m\mu$ , but strongly absorbs at 440  $m\mu$ . This interference can be eliminated by simply adding a small amount of phosphoric acid to the sulfuric acid-chloride stripping solution. The iron forms the colorless phosphate complex and the interference is eliminated. It was found that two extractions each with 5 ml of 3 F sulfuric acid containing 6 g/liter sodium chloride are sufficient to remove all the free PAR from the ethyl acetate extracts. The absorbance can now be measured at 440  $m\mu$  thus, approximately doubling the sensitivity.

Re-extraction into Aqueous Sulfuric Acid. Knowledge of the action of chloride on the extraction of the palladium-PAR complex leads to a further modification which allows for increased sensitivity. This modification is made possible by utilizing the action of mercury(II), and permits, in a very simple fashion, the concentration of the green complex in an extremely small final volume. After all free PAR has been removed, the ethyl acetate layer is shaken with an aqueous solution of mercuric sulfate or nitrate. The mercury(II) complexes all of the free chloride and deprives the green palladium complex of its coordinated chloride. Under these conditions, the now chloride free palladium-PAR complex is formed and moves immediately into the aqueous phase. Thus, for example, the green complex dissolved in 25 ml of ethyl acetate can readily be concentrated into 2-3 ml of aqueous solution by a single step.

Destruction of the Palladium-PAR Complex. This modification is based on the action of dimethylglyoxime encountered during an earlier

experiment.

At one phase of the investigation, an attempt was made to achieve a single-step separation of palladium from all other metal ions by precipitation with dimethylglyoxime, in the presence of nickel as the scavenger. This attempt failed because after dissolution of the palladium-dimethylglyoxime complex in 3 F sulfuric acid, no green color was developed upon the addition of PAR. Palladium is obviously still so strongly coordinated to the dimethylglyoxime that no reaction with PAR takes place. This indicates that the dissolution of the insoluble palladium-dimethylglyoxime complex in acids is most probably due to the formation of a partially protonated soluble complex rather than to dissociation under the influence of the acid. While the idea of separation by precipitation was abandoned, the use of dimethylglyoxime offered another interesting possibility to further increasing the sensitivity. When dimethylglyoxime is added to an aqueous solution containing the green palladium-PAR complex, decomposition of this complex occurs rather rapidly and the color of the free PAR appears. Since the absorptivity of the free PAR at its peak at 410 m $\mu$  is about 1.5 times that of the palladium-PAR at 416 m $\mu$ , measuring the absorbance of the liberated PAR allows for a further increase in sensitivity by a factor of 1.5. Details for this approach are given in Procedure V.

Separation of Palladium. During the preliminary investigations, several metals caused an interference that could not be eliminated by masking. The only solution in this case appeared to be the separation of the interfering metals or a separation of palladium from the interfering metals. The latter approach was chosen and the chloroform

extraction of the palladium-dimethylglyoxime complex was investigated. After several modifications a procedure was developed which allows for the separation of palladium from many other metals. This procedure is described in detail in the next section of this chapter.

### Procedures

#### Procedure I (Non-extractive Method)

Transfer an aliquot of the chloride-free sample solution to a 25-ml volumetric flask and add 4.2 ml of concentrated sulfuric acid. (Note 1.) Add 5.00 ml of PAR solution ( $10^{-3}$  F), dilute to mark with deionized water and allow to stand for 15 minutes.

Place an identical aliquot of the sample solution in a 25-ml volumetric flask, add 4.2 ml of concentrated sulfuric acid and dilute to mark with deionized water. Using this solution, set 100 percent transmittance at 580 m $\mu$  and then measure the absorbance of the sample. (See Note 2.)

Prepare a calibration curve by placing exactly known amounts of palladium standard solution into 25-ml volumetric flasks and treat as described above. Measure the absorbance at 580 m $\mu$ , using deionized water as the reference.

#### Notes

1) With low amounts of palladium present, a smaller volumetric flask may be used. The amount of sulfuric acid should then be reduced accordingly so that after dilution to the final volume, the solution is approximately 3 formal in that acid. If insoluble sulfates precipitate, filter before proceeding further.

2) If the solution after addition of sulfuric acid is colorless or if it is known that the colorants present do not absorb at 580  $m\mu$ , deionized water may be used to set 100 percent transmittance.

#### Procedure II (Extractive Approach)

Transfer the chloride-free solution or an aliquot of it to a 60-ml separatory funnel, add 5 ml of concentrated sulfuric acid, 5 ml of PAR stock solution ( $10^{-3}$  F), dilute to approximately 30 ml with deionized water and allow to stand for 15 minutes. Add 1 ml of a 1 F sodium chloride solution and immediately extract with a 15-ml and then a 10-ml portion of ethyl acetate saturated with 3 F sulfuric acid. (See Note 1.) Combine the extracts in a 25-ml volumetric flask and dilute to mark with sulfuric acid saturated ethyl acetate. Use deionized water to set the 100 percent transmittance and measure the absorbance at 616  $m\mu$ .

Prepare a calibration curve by placing exactly known amounts of standard palladium solution II in 60-ml separatory funnels and treat as described above. Plot the data in the usual manner to obtain the calibration curve.

#### Notes

1) If low amounts of palladium are present, smaller volumes of ethyl acetate may be used so that the palladium-PAR complex will be more concentrated. It may also be desirable to dilute to a smaller aqueous volume before the extraction step, then however, the amount of sulfuric acid should be reduced so that the final solution is 3 formal in that acid.

### Procedure III

Treat the chloride-free sample solution or an aliquot of it in the same manner as in Procedure II up to and including the extraction. Combine the extracts in a separatory funnel and wash with two 5-ml portions of stripping solution A, (sodium chloride in sulfuric acid, see Chapter V), discarding the aqueous phases. Place the washed organic phases in a 25-ml volumetric flask and dilute to mark with ethyl acetate saturated with sulfuric acid. Using deionized water, set the 100 percent transmittance and measure the absorbance at 440 m $\mu$ .

Prepare a calibration curve by placing exactly known amounts of standard palladium solution II in 60-ml separatory funnels and treat as described above. Plot the data in the usual manner to obtain the calibration curve.

### Procedure IV (Re-extractive Technique)

Treat the chloride-free sample solution or an aliquot of it in the same manner as in Procedure III up to and including the stripping step. Treat the organic layer in the separatory funnel with a 2-ml portion of stripping solution B (mercuric sulfate in 3 F sulfuric acid, see Chapter V) and drain the aqueous layer into a 5-ml volumetric flask. Repeat with a second 2-ml portion of stripping solution B and again drain into the 5-ml volumetric flask. Dilute the combined aqueous phases with 3 F sulfuric acid to mark. Use deionized water to set the 100 percent transmittance and then measure the absorbance at 416 m $\mu$ .

Prepare a calibration curve by placing exactly known amounts of standard palladium solution II in 60-ml separatory funnels and treat as described above. Plot the data in the usual manner to obtain the

calibration curve.

#### Procedure V (Free PAR Technique)

Treat the chloride-free sample solution or an aliquot of it in the same manner as in Procedure IV up to and including the stripping step. Add 3-5 drops of saturated dimethylglyoxime solution to the combined aqueous phases, dilute to mark with 3 F sulfuric acid and allow to stand for 10 minutes. Use deionized water to set the 100 percent transmittance and measure the absorbance at 410 mμ.

Prepare a calibration curve by placing exactly known amounts of standard palladium solution II in 60-ml separatory funnels and treat as described above. Plot the data in the usual manner to obtain the calibration curve.

#### Procedure VI (Palladium Separation)

Transfer an aliquot of the sample solution to a 250-ml separatory funnel, add 2 ml of concentrated nitric acid and dilute to approximately 100 ml with deionized water (see Note 1). Add 3 ml of 0.1 F dimethylglyoxime solution and allow to stand for one hour. Extract the aqueous solution with four portions of chloroform (50, 25, 15, and 10 ml, respectively). Combine the chloroform extracts in a 300-ml Erlenmeyer flask and evaporate to dryness on a water bath (see Note 2). To the residue add 5 ml of sulfuric acid and 15 drops of 70 percent perchloric acid and heat until white fumes appear. Continue heating for about 10 minutes. Cool, transfer to a 60-ml separatory funnel, and continue according to Procedure II.

#### Notes

- 1) If the sample contains gold, the amount of palladium present

should not exceed 50  $\mu\text{g}$ . To prevent reduction of the gold, saturate the solution with ammonium chloride and have an excess of the solid salt present. If, in addition to gold, silver is present, it is recommended to add the sample aliquot to the solution saturated with ammonium chloride containing an excess of the solid salt. This sequence of addition facilitates the redissolving of the silver chloride initially formed, especially if large quantities of silver are present. If sizable amounts of platinum are present, ammonium chloroplatinate forms and the precipitate interferes in the extraction. This difficulty can be overcome by replacing ammonium chloride with lithium chloride.

2) If the combined chloroform extracts show a yellow coloration due to coextraction of some gold-chloro complexes, wash with several small portions of a saturated aqueous solution of ammonium chloride containing a few drops of nitric acid prior to evaporation of the chloroform.

#### Results and Discussion

Figure 13 is a calibration curve obtained by following Procedure II for the determination of palladium in 3 F sulfuric acid. It shows a linear relationship between the absorbance and concentration from 0 to at least 4.56  $\mu\text{g}$  palladium per milliliter. The molar absorptivity calculated from this data is  $9.50 \times 10^{+3}$  liters/mole-cm. The sensitivity as expressed by Sandell (161) is .012  $\mu\text{g}/\text{cm}^2$ .

Figure 14 shows calibration curves obtained by following Procedure II, IV, and V. The line designated A is the normal calibration curve for Procedure II measured at 616 m $\mu$ . Lines B and C are calibration curves obtained by following Procedures IV and V, respectively and show

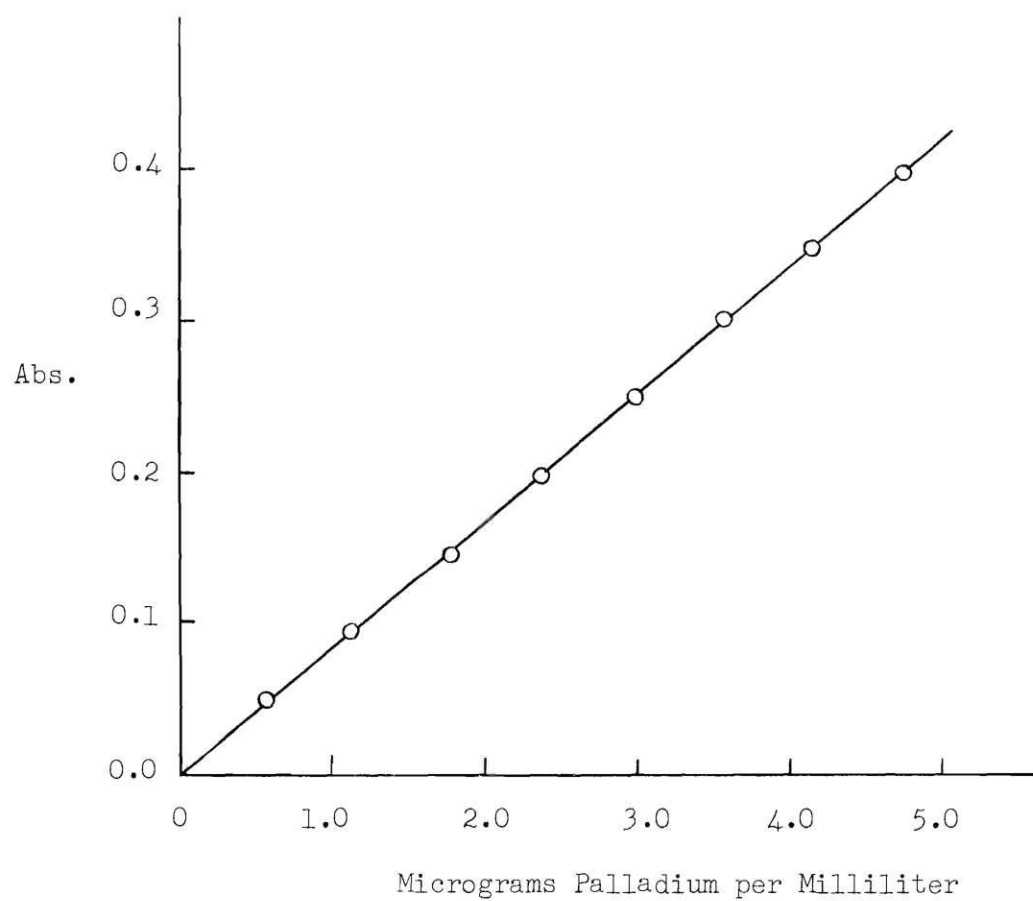


Figure 13. Palladium Calibration Curve for Procedure II



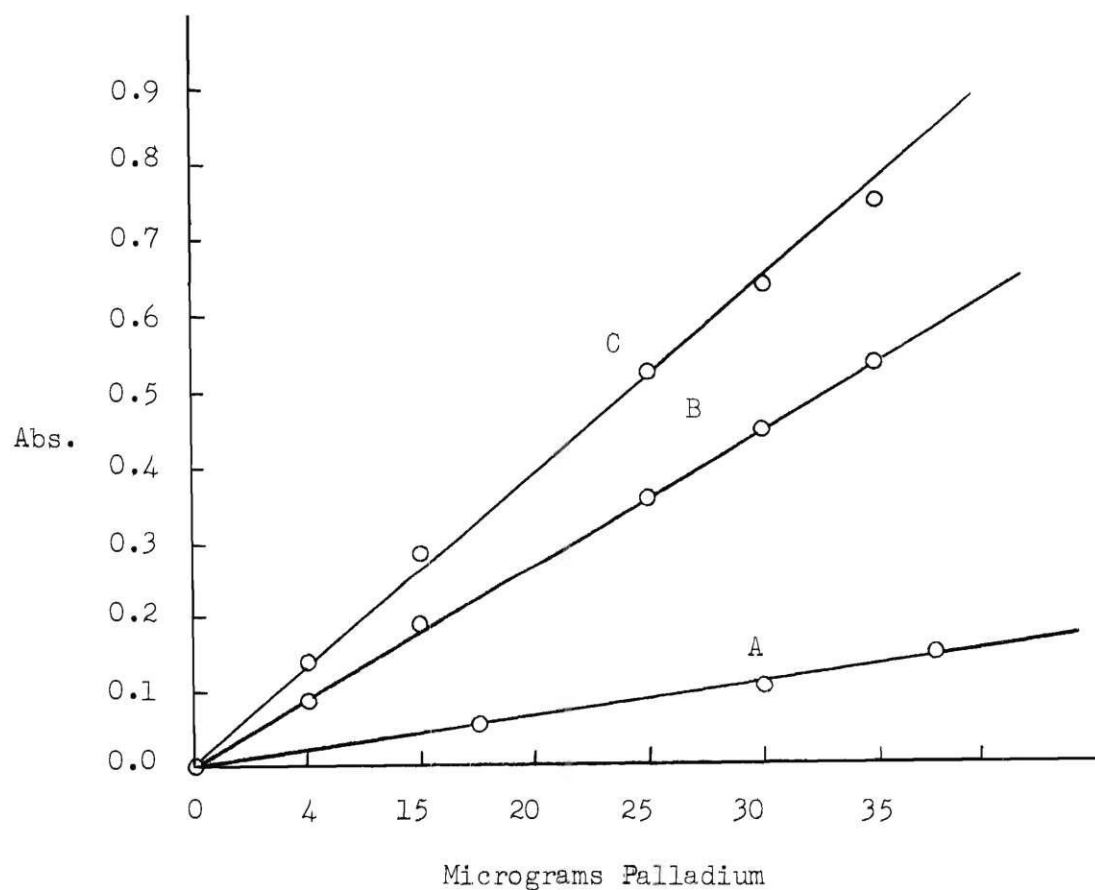


Figure 14. Calibration Curves Applicable to Modified Procedures

- A Procedure III, 25 ml Ethyl Acetate Phase; Absorbance Measured at 618  $m\mu$
- B Procedure V, 10 ml Aqueous Phase; Absorbance Measured at 440  $m\mu$
- C Procedure VI, 10 ml Aqueous phase; Absorbance Measured at 410  $m\mu$

a linear relationship between absorbance and concentration from 0 to 2.97  $\mu\text{g}$  palladium per milliliter. The palladium-PAR complex at 440  $\text{m}\mu$  has a molar absorptivity of  $1.86 \times 10^4$  liters/mole-cm. The sensitivity as expressed by Sandell (161) is  $0.0057 \mu\text{g}/\text{cm}^2$ . Free PAR in 3  $\text{F}$  sulfuric acid shows a molar absorptivity of  $2.37 \times 10^4$  liters/mole-cm and the Sandell "sensitivity" is  $0.0045 \mu\text{g}/\text{cm}^2$ .

Table 7 presents the results for the determination of palladium according to Procedure II. Results are given for solutions containing only palladium and for solutions that also contain other metals. The first entries in this table show a quite satisfactory accuracy and precision of the method with palladium alone. When evaluating the data, one should consider that under the experimental conditions a variation of  $\pm 0.003$  absorbance units corresponds to approximately  $\pm 1 \mu\text{g}$  palladium.

Several metals (*i.e.*, lead, calcium, barium) form insoluble sulfates. One attempt to eliminate the formation of these precipitates was to operate in 6  $\text{F}$  perchloric acid instead of sulfuric acid. The palladium-PAR complex is formed under these conditions, but extraction with ethyl acetate is not possible since it is completely miscible with 6  $\text{F}$  perchloric acid. However, the insoluble sulfates formed do not cause any interference since the ethyl acetate extraction can be accomplished without even a prior filtration. Lead has been studied in ratios as high as 10,000:1, and was found to cause no interference. If, however, it were necessary to determine palladium in the presence of even larger proportions of lead, as in the case where fire assay techniques are employed, difficulties might be encountered. Beamish (8) has reported losses of palladium due to coprecipitation with large amounts of lead sulfate. He

Table 7. Results of Palladium Determinations According to Procedure II

$\mu\text{g}$ Palladium		Diff.	Metal Ion	Mole Ratio
Added	Found		M added	M: Pd
59.4	59.4	0.0	-----	-----
	58.4	-1.0	-----	-----
	58.4	-1.0	-----	-----
	58.6	-0.8	-----	-----
	59.4	0.0	-----	-----
	58.9	-0.5	-----	-----
	58.6	-0.8	-----	-----
	58.9	-0.5	Li <sup>+1</sup>	2000:1
	58.9	-0.5	Na <sup>+1</sup>	2000:1
	58.9	-0.5	K <sup>+1</sup>	2000:1
	57.8	-1.6	Be <sup>+2</sup>	2000:1
	57.3	-2.1	Mg <sup>+2</sup>	2000:1
	59.4	0.0	Ca <sup>+2</sup>	2000:1
	57.8	-1.6	Sr <sup>+2</sup>	2000:1
	57.8	-1.6	Ba <sup>+2</sup>	2000:1
	57.8	-1.6	Y <sup>+3</sup>	2000:1
	57.3	-2.1	La <sup>+3</sup>	2000:1
	59.4	0.0	Ti <sup>+4</sup>	2000:1
	59.4	0.0	Zr <sup>+4</sup>	2000:1
	57.8	-1.6	V <sup>+4</sup>	2000:1
	58.4	-1.0	Cr <sup>+3</sup>	2000:1
	57.8	-1.6	Mo <sup>+6</sup>	2000:1
	57.8	-1.6	W <sup>+6</sup>	2000:1
	58.4	-1.0	Mn <sup>+2</sup>	2000:1
	59.4	0.0	Fe <sup>+3</sup>	2000:1
	59.4	0.0	Fe <sup>+3</sup>	10000:1
	58.9	-0.5	Co <sup>+2</sup>	2000:1
	58.4	-1.0	Co <sup>+2</sup>	10000:1
	58.8	-0.6	Ni <sup>+2</sup>	2000:1

Table 7. Continued

<u>μg Palladium</u>			Metal Ion	Mole Ratio
Added	Found	Diff.	M added	M: Pd
59.4	58.4	-1.0	Cu <sup>+2</sup>	10000:1
	58.9	-0.5	Al <sup>+3</sup>	2000:1
	58.9	-0.5	Ga <sup>+3</sup>	2000:1
	58.9	-0.5	In <sup>+3</sup>	2000:1
	58.9	-0.5	Tl <sup>+1</sup>	2000:1
	58.4	-1.0	Tl <sup>+3</sup>	2000:1
	58.4	-1.0	Sn <sup>+4</sup>	2000:1
	59.4	0.0	Pb <sup>+2</sup>	2000:1
	58.9	-0.5	Pb <sup>+2</sup>	10000:1
	57.8	-1.6	As <sup>+3</sup>	2000:1
	58.4	-1.0	As <sup>+5</sup>	2000:1
	57.8	-1.6	Bi <sup>+3</sup>	2000:1
	57.3	-2.1	Ce <sup>+3</sup>	2000:1
	58.4	-1.0	Th <sup>+4</sup>	2000:1
	58.4	-1.0	Nd <sup>+3</sup>	2000:1
	57.8	-1.6	UO <sub>2</sub> <sup>+2</sup>	2000:1
	59.4	0.0	Ru <sup>+2</sup>	200:1
29.7	29.1	+0.6	Ru <sup>+2</sup>	2000:1
59.4	60.0	+0.6	Os <sup>+3</sup>	200:1
59.4	61.1	+1.7	Ir <sup>+3</sup>	200:1
29.7	30.3	+0.6	Ir <sup>+3</sup>	200:1
59.4	57.8	-1.6	Rh <sup>+3</sup>	200:1
59.4	60.0	+0.6	Pt <sup>+4</sup>	200:1
29.7	31.5	+1.8	Pt <sup>+4</sup>	2000:1
59.4	58.9	-0.5	Zn <sup>+2</sup>	2000:1
	58.9	-0.5	Zn <sup>+2</sup>	10000:1
	57.8	-1.6	Cd <sup>+2</sup>	2000:1
	61.1	+1.7	Cu <sup>+2</sup> , Co <sup>+2</sup> , Ni <sup>+2</sup> , Fe <sup>+3</sup>	2000:1
	60.6	+1.2	Co <sup>+2</sup> , Ni <sup>+2</sup> , Fe <sup>+3</sup>	2000:1

Table 7. Continued

<u>μg Palladium</u>			Metal Ion	Mole Ratio
Added	Found	Diff.	M added	M: Pd
59.4	57.8	-1.6	Pb <sup>+2</sup>	2000:1
	58.6	-0.8	Au <sup>+3</sup>	20:1
	57.3	-2.1	Au <sup>+3</sup>	25:1

has developed a method of separating microgram quantities of palladium from 15 to 30 grams of lead. This approach utilizes a chloroform extraction of the palladium dimethylglyoxime complex. The application of this technique in connection with large amounts of several metals has been investigated and is discussed in detail in a later section of this chapter.

Several metals were found to cause interferences in the extractive technique as described in Procedure II. Some of these metals require a special treatment to prevent their interference. The results of the determination of palladium in the presence of metals that require a special modification are presented in Table 8 and are discussed in the following section.

Tin(II) interferes if added to a solution containing PAR and palladium. This interference is due to reduction of the chromogenic reagent and probably some of the palladium. This influence of tin(II) is of academic interest only since tin in this oxidation state will never be present under the conditions of an actual analysis.

Cerium(IV) causes low results in the recovery of palladium; however,

Table 8. Results of Palladium Determinations in the Presence of Elements Requiring Special Modifications of the Standard Procedures

$\mu\text{g}$ Palladium		Diff.	Metal Ion M Added	Mole Ratio M: Pd	
Added	Found				
59.4	58.9	-0.5	V <sup>+5</sup>	1000:1	} a
	58.9	-0.5	V <sup>+5</sup>	2000:1	
	59.4	0.0	Sb <sup>+5</sup>	2000:1	} b
	59.4	0.0	Sb <sup>+5</sup>	2000:1	
	58.6	-0.8	Sb <sup>+5</sup>	2000:1	
	58.9	-0.5	Hg <sup>+2</sup>	2000:1	} c
	58.9	-0.5	Hg <sup>+2</sup>	2000:1	
29.7	29.1	-0.6	-----	-----	} d
50.4	49.9	-0.5	-----	-----	
59.4	58.9	-0.5	-----	-----	
	59.4	0.0	-----	-----	
	58.9	-0.5	-----	-----	
	58.9	-0.5	Cu <sup>+2</sup> , Ni <sup>+2</sup>	2000:1	
	57.3	-2.1	Mn <sup>+2</sup> , Zn <sup>+2</sup> , Cd <sup>+2</sup>	2000:1	
			V <sup>+5</sup> , Cr <sup>+3</sup>		
	58.6	-0.8	Ag <sup>+1</sup> , Hg <sup>+2</sup>	2000:1	
	58.9	-0.5	Au <sup>+3</sup>	200:1	
			Au <sup>+3</sup>	200:1	
	58.6	-0.8	Ag <sup>+2</sup>	2000:1	
	59.4	0.0	Au <sup>+3</sup>	2000:1	
29.7	29.7	0.0	Au <sup>+3</sup>	6000:1	
59.4	59.4	0.0	Ag <sup>+1</sup>	20,000:1	
89.1	88.5	-0.6	-----	-----	

a. Samples were cooled to room temperature before addition of PAR.

b. Ethyl acetate extract was washed with 0.05  $\text{F}$  NaCl before final

dilution to 25 ml.

- c. Chloride added in amounts to completely combine with mercury and to provide a slight excess for the formation of the palladium-PAR-chloro mixed complex.
- d. Palladium separated from interfering metal by extraction of the dimethylglyoxime complex.

this is not a serious interference since it can easily be eliminated by the reduction of cerium(IV) to cerium(III) by the addition of hydrogen peroxide.

Silver interferes in the determination of palladium by Procedure II and the mechanism of this interference is quite interesting. Although the palladium-PAR complex forms readily in the presence of silver, silver chloride precipitates upon the addition of the chloride necessary for the extraction of the palladium-PAR complex. It is therefore necessary to determine the palladium content by the non-extractive approach described in Procedure I.

Mercury(II) interferes in a manner similar to that of silver. The green palladium-PAR complex is formed readily, however, the mercury-chloro complexes that are formed upon the addition of chloride are so stable that no chloride is available for the formation of the mixed palladium-PAR-chloro complex which is necessary for extraction. This problem can be eliminated by adding chloride in a slight excess over that required for complete complexing with mercury. (See Table 8.) The interference due to mercury is not a serious problem since this metal is usually absent in materials commonly analyzed for palladium. If mercury is present in the original sample, it is easily removed by roasting.

The interference of vanadium(V) is due to a heat-promoted reaction with PAR. If PAR is added to a solution containing palladium and vanadium(V), being still warm due to the preceding addition of concentrated sulfuric acid, the chromogenic agent undergoes a decomposition and no palladium-PAR complex is formed. If, however, the solution is cooled to



room temperature or lower before adding the PAR, no interference is observed. The fact that the interference is due to a reaction between vanadium and PAR rather than vanadium and palladium, can be demonstrated in the following manner. If a solution containing palladium, vanadium(V) and sulfuric acid is boiled, cooled under tap water, and PAR added, correct results for palladium are obtained. (See Table 8.)

Antimony(III) and (V) interfere by the formation of red PAR complexes that are partially co-extracted with the palladium-PAR complex into ethyl acetate. These interferences can be eliminated by washing the combined ethyl acetate extract with an aqueous sodium chloride solution (about .01 F). This washing lowers the acidity, causing the antimony-PAR complexes to decompose, and the interfering metal ions pass into the aqueous phase (see Table 8).

Gold interferes when present in ratios greater than 20:1. If larger proportions are encountered, a prior separation is required. A number of methods for separating gold and palladium, ranging from selective reduction to extraction of the gold, have been investigated. The separation that proved to be most satisfactory was an extraction of palladium. This method is a modification of the previously mentioned chloroform extraction of the palladium-dimethylglyoxime complex (8). Young (162) has described a separation of palladium from platinum and gold using this extraction. He reported that gold remains in the aqueous phase if a small amount of nitric acid is added to the solution prior to the addition of dimethylglyoxime. However, he does not mention the amount of gold that can be present without interfering. When attempting this separation with large molar ratios of gold to palladium (200:1 and higher),

a heavy precipitate of metallic gold was obtained which interfered with the extraction of the palladium-dimethylglyoxime complex. However, if the aqueous solution containing gold and palladium is saturated with ammonium chloride before the addition of dimethylglyoxime, no reduction of gold occurs and the palladium-dimethylglyoxime complex is completely extracted into chloroform. Only a small amount of gold chloride is co-extracted, but this amount is well below that causing interference in the palladium determination. The effect of dimethylglyoxime on the palladium-PAR reaction has already been discussed and it is obvious that excess dimethylglyoxime as well as its palladium complex must be completely destroyed so that palladium can react with PAR. Beamish (8) achieves this destruction in the following manner. The residue after evaporation of the chloroform is treated with nitric and sulfuric acid and the solution heated to white fumes. After cooling, water is added and the solution again heated to fuming. Addition of water and fuming must be repeated several more times to assure complete elimination of all nitrous oxides. This tedious procedure can be shortened considerably by fuming only once, cooling, and adding a spatula tip of urea, which completely eliminates interfering nitrous oxides. An even simpler approach is to evaporate the chloroform solution to dryness in an Erlenmeyer flask, to add 6 ml of sulfuric acid and 15 drops of concentrated perchloric acid, to heat to white fumes for about 10 minutes, to cool and then to continue according to Procedure II. Results obtained with pure palladium solutions and with gold at ratios as high as 6000:1 are presented in Table 8. If sizable amounts of platinum are present ammonium chloroplatinate forms and the precipitate interferes in the chloroform extraction of the

palladium-dimethylglyoxime complex. This difficulty can be readily overcome by replacing ammonium chloride with lithium chloride.

The separation of palladium by this extraction also offers advantages with solutions containing silver or mercury or both. The effect of these two metals has been previously described. Table 8 shows also the results obtained with solutions containing silver in ratios as high as 20,000:1. The silver chloride that is initially formed redissolves in the saturated ammonium chloride solution and the palladium separation via extraction proceeds without interference.

Niobium and tantalum precipitate in 3 F sulfuric acid unless complexed with citrate or tartrate. At the concentrations of tartrate and citrate required to keep these metals in solution, a partial reduction of the palladium occurs. Several attempts at masking these interfering metals failed and a separation had to be applied. The simplest way to achieve this separation is to add silver as a scavenger, to reduce both silver and palladium with ascorbic acid and isolate the metallic precipitate by filtration with a sintered porcelain filter crucible. The precipitate in the crucible and at the walls of the precipitation vessel is readily dissolved by first applying some nitric acid, then a small volume of aqua regia. The combined solutions are fumed with sulfuric acid and the solution thus obtained may then be subjected to any of the methods previously described. Since niobium and tantalum will hardly accompany palladium in an actual sample, no more emphasis was placed on this problem. Correct results for palladium were obtained in one trial containing niobium and tantalum in mole ratios of 1600:1 and 600:1, respectively.

If it is desired to carry out the determination of palladium in a strongly acidic medium, Procedure II is recommended. In Procedure I it is necessary to prepare a blank for each sample in order to prevent interferences due to the absorbance of any colorants that may be present. The extraction step in Procedure II does not require much additional time and eliminates the necessity of a special blank solution.

## CHAPTER VIII

### EVALUATION OF THE METHODS DEVELOPED

#### Introduction

In Chapter III the requirements for an ideal spectrophotometric method were briefly discussed. It was pointed out that such a method should allow the determination of a metal within a matrix containing any or all of the other elements or at least those elements that are expected to accompany that metal in natural or artificial products. The method should also possess a high level of sensitivity and should involve as simple a procedure as possible.

The review of existing methods for the determination of palladium (see Chapter III) has revealed that most of these leave much to be desired, and that relevant investigations may well be able to improve the situation. Such investigations were initiated, and the methods developed during this research and reported in the present thesis will now be discussed and reviewed with special consideration as to how close they approach the ideal.

#### Method at pH 7.0

As seen in Chapter VI, this method yields very good results even in the presence of many foreign metal ions.

The time required for a determination is quite reasonable and the procedure is straight forward. The colored complex formed between palladium and PAR is very stable and has a high absorptivity. The utilization

of a masking solution containing EDTA, sodium citrate and potassium chloride allows the determination of palladium in the presence of large amounts of lithium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, aluminum, arsenic(III) and (V), scandium, yttrium, manganese, tungsten, zinc, cadmium, mercury(II), gallium, indium, thallium(I) and (III), tin(IV), lead, antimony(III) and (V), bismuth, selenium, lanthanum, praseodymium, neodymium, cerium(III), nickel, copper, chromium(III) and (VI), vanadium(IV), iron(III), ruthenium, and osmium. The uranyl ion requires the addition of sodium carbonate to mask its reaction with PAR.

Niobium, tantalum, cobalt, gold, silver, iridium, platinum, and vanadium(V) are not masked and interfere in the method. In the absence of these metals this method offers the possibility for rapid, accurate and sensitive determination of palladium.

With respect to the ideal method, however, this approach leaves something to be desired. Of the metals that cause an interference gold, silver, iridium, cobalt and platinum are especially serious since these metals will often be associated with palladium in either natural or man-made materials. The need for still an improved method is apparent and additional investigations were concluded.

#### Method in 3 F Sulfuric Acid

It is possible to form a green palladium-PAR complex in 3 F sulfuric acid and the absorbance can be measured in the aqueous medium. The time required for the complete formation of this complex is about 15 minutes. Problems occur, however, if other colored ions are present. A special blank containing an identical aliquot of the sample but no PAR can be used to eliminate some of these interferences. However, a

modification of this method provides an effective means of eliminating such interferences. The green complex can easily be extracted into ethyl acetate. This extraction not only excludes the interference of some metals but it also allows for the concentration of the palladium-PAR complex. Since the extraction is straight forward and simple, very little extra time is required for this additional step.

Excellent results for the determination of palladium were obtained by application of this approach described as Procedure II in Chapter VII. Palladium can be determined in the presence of large amounts of lithium, potassium, sodium, beryllium, magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, titanium, zirconium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, cadmium, aluminum, gallium, indium, thallium(I) and (III), tin(IV), lead, arsenic(III) and (V), bismuth, praseodymium, neodymium, thorium, uranium, platinum, iridium, osmium, and rhodium.

Gold when in mole ratios less than 20:1 has no interference. When larger amounts are present a separation of the palladium via a dimethylglyoxime extraction is necessary. This extraction requires about two hours, but it completely eliminates the interference caused by gold.

Silver, mercury(II), vanadium(V), and antimony(III) and (V) interfere in the extractive method for palladium. However, these interferences are easily eliminated by the application of one of the simple modifications described in Chapter VII. Niobium and tantalum interfere in the determinations of palladium, but this interference is not serious since these metals will hardly ever be present in a sample to be analyzed for palladium, and, even if they are present, their separation is quite

easy.

The modified methods described as Procedures III, IV, and V (Chapter VII) are all useful for improving the overall sensitivity of the determination of palladium with PAR. These and the previously mentioned modifications also have a rather unique feature. It is not necessary to decide in advance which procedure (I through V) should be applied. When analyzing samples with completely unknown contents of palladium, one may proceed as described in Procedure I or more preferably Procedure II. If in the latter case the absorbance measurements or visual inspection indicates that a greater sensitivity is required, the free PAR may be stripped from the ethyl acetate, according to Procedure III, and the sensitivity approximately doubled by measuring the absorbance at 440 m $\mu$ . If a further increase of sensitivity is desired, Procedure IV may be used and the palladium-PAR complex concentrated in a small aqueous phase. Finally, Procedure V may be applied and the PAR which is liberated from its palladium complex by dimethylglyoxime measured at 410 m $\mu$ . If calibration curves have been prepared for each of these procedures, it is possible to start with any one of the procedures and continue from one modification to the next, stopping when a satisfactorily high absorbance reading is obtained.

With the appropriate application of one of the methods described, it should be possible to determine palladium in the presence of any other metal commonly associated with it.

With respect to the ideal situation, these methods approach very closely the previously mentioned requirements. The procedures described give reliable results, are relatively simple, highly sensitive, and selective and do not require extensive amounts of time.



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## VITA

Jackson Earl Hicks was born on December 12, 1934, in Fruitland Park, Florida, to Wilmer Jackson Hicks and Vivian Peters Hicks. He attended high school at Summerlin Institute in Bartow, Florida and was graduated in June, 1953. He attended the University of Florida, Gainesville, Florida; and Erskine College, Due West, South Carolina, and received a B.A. degree in Chemistry from the latter in June, 1958.

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